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Organic Intermetallic Derivatives of Tin
and
Copperacetylide Complexes

by

D. Blake

A Thesis submitted for the Degree of Doctor of
Philosophy in the University of Durham
1958.

Acknowledgements

The author would like to record his sincere appreciation for the guidance and encouragement given by Professor G.E. Coates during the course of the present investigation. The author is also indebted to Dr. F. Glockling for his constant advice and to the Department of Scientific and Industrial Research for a grant.

Memorandum

The work described in this thesis was carried out at the Durham Colleges in the University of Durham between September 1955 and October 1958. This work has not been submitted for any other degree and is the work of the author, except where acknowledged by reference.

The work carried out by the author consisted of two separate investigations, the results of which are given in Parts I and II of this thesis.

D. Blake
23/5/59.

Summary

Part I

Organic Intermetallic Derivatives of Tin

Some reactions of trialkyltin alkali metal derivatives were studied with the view to their use as synthetic reagents for the introduction of the trialkyltin radical into other molecules and ultimately for syntheses of compounds in which tin would be covalently bonded to a metal from another chemical group.

The reactions studied in ether-like solvents indicated that reaction between trialkyltin lithium compounds and organo-metallic halides led either to occurrence of metal-halogen exchange reactions or dissociation of the trialkyltin lithium. In the former case the symmetrical organo-dielement compounds were formed, *e.g.* hexamethylditin, cacodyl; and in the latter case, the alkyl lithium, produced by dissociation, reacted with the organo-metallic halide resulting in replacement of the halogen with an alkyl group. When, however, reaction between a trialkyltin lithium and an alkyl halide was carried out the expected reaction occurred, since, in this case, the reaction between the halide and any alkyl lithium produced by dissociation would be relatively slow, thus enhancing the chance of reaction between the alkyl halide and the trialkyltin group.

Reactions carried out with elements from Group VI, sulphur and selenium, led to formation of the desired compounds methyltrimethyltin sulphide and methyltrimethyltin selenide. The latter compound contained a tin-selenium bond which does not appear to have been reported previously. In these reactions the trialkyltin radical was present in cationic form (as the bromide) and the Group VI elements in anionic form, so that metal-halogen exchange reactions would be most unlikely to occur.

As the reactions with tin in cationic form had been successful a reaction between dimethylarsenic sodium and trimethyltin bromide was studied in liquid ammonia. However, results from this reaction again indicated that formation of the symmetrical di-element compounds occurred rather than combination of the trialkyltin radical with the dimethylarsenic group.

As the reactions studied with trialkyltin alkali metal derivatives in ether-like solvents had shown that they behaved in a complex manner with a variety of reagents attention was directed to the rather limited use of liquid ammonia as a solvent for effecting reactions of the type discussed. In this solvent most organo-metallic halides are rapidly ammonolysed, tin and gallium however being exceptions, the reaction between trimethyltin sodium and dimethylgallium chloride mon-ammine was investigated. There was no indication that a tin-gallium bond was formed, tin being recovered as hexamethylditin and gallium as dimethylgallium amide.

Part II

Copperacetylide Complexes

Some new co-ordination complexes of copperacetylides and of silveracetylides, which appear hitherto unknown, were prepared and some of their properties investigated.

In the series nitrogen, phosphorus, arsenic it was found that the order of stability of the co-ordination complexes was $N \ll P > As$, those of phosphorus being by far the most stable. An important difference between the alkyl- and aryl-copperacetylide triethyl- phosphine complexes was observed in their behaviour in solution, in which the former dissociated $(R\text{-}C\equiv C\overset{-}{Cu}\text{-}\overset{+}{P}(C_2H_5)_3 \rightleftharpoons R\text{-}C\equiv CCu + (C_2H_5)_3P)$. Such dissociation was also exhibited by the phenylsilver-acetylide-triethylarsine and -*iso*-propylamine complexes. The alkylcopperacetylide complexes oxidised rapidly in air, whereas the corresponding arylcopperacetylide compounds were much more stable. There was no indication that co-ordination of the metal acetylides occurred with sulphur co-ordinating reagents.

Molecular weight determinations, where possible, showed that the co-ordination complexes were generally highly associated, the alkyls more so than the aryls, but the silver compounds less so than the corresponding copper co-ordination complexes. In the case of *t*-butylcopperacetylide, which is soluble in organic solvents, molecular weight determinations confirmed earlier results, and showed that the copperacetylide was also highly associated.

The relative stability of the copper- and silver-acetylides and their co-ordination compounds has been discussed and attributed to co-ordination of the metal with an acetylene group from another molecule, in accordance with the conclusions of earlier work on t-butylcopperacetylide. Any formation of a complex R-C≡C.ML (M=Cu or Ag, L = ligand) must be the result of successful competition between the M-acetylene co-ordination, which leads to the polymerisation of R-C≡CM itself, and the co-ordination -M-L. Since the acetylides are, in general, only depolymerised by those ligands known to be the strongest donors to copper^{I} and silver^{I} (namely aliphatic tertiary phosphines), and since the resulting compounds R-C≡CM-L are themselves associated in solution, presumably by metal-acetylene group interaction, the last must be supposed to be very strong.

Part I

Organic Intermetallic Derivatives of Tin

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Discussion of Results (cont.)

1. Introduction

The main purpose of the present work was to study the use of alkali metal derivatives of the trialkyltin radical (Alk_3SnM) as synthetic reagents for the introduction of the trialkyltin radical into other molecules, and particularly into combination with other metals. It was anticipated by analogy with the already known reaction[1] between tri-n-butyltin lithium and n-butyl iodide,

$$(n\text{-}C_4H_9)_3SnLi + n\text{-}C_4H_9I = (n\text{-}C_4H_9)_4Sn + LiI,$$

and numerous metathetical reactions of similar type carried out in liquid ammonia,[2-4] that reaction with alkyl-metal halides would afford desired compounds of the type $Alk_3Sn\text{-}Metal\text{-}Alk_{n-1}$ (n = covalency of the metal concerned).

Although much more information is available about the formation and reactions of alkali metal derivatives of trialkyl (and even dialkyl)-tin in liquid ammonia, attention was primarily directed to the use of ether solvents since most of the organic metal halides that might be studied are rapidly ammonolysed in liquid ammonia, e.g., cacodyl chloride trimethylchlorsilane.

Three methods for obtaining alkali metal derivatives of the trialkyltin radical were studied:-

a) Preparation of the alkali metal derivative in liquid ammonia, by known methods, followed by replacement of the ammonia by ether, e.g.,

$Alk_3SnBr + 2Na = Alk_3SnNa + NaBr.$

b) The use of an ether such as tetrahydrofuran, which has a stronger solvating effect than that of diethyl ether on alkali metal ions, and facilitates the formation of a variety of alkali metal derivatives of organic compounds, to carry out a reaction essentially similar to a) above.

c) Gilman and Rosenberg's method,[1] starting from stannous chloride and using diethyl ether as solvent, e.g.,

$3\ \underline{n}\text{-}C_4H_9Li + SnCl_2 = (\underline{n}\text{-}C_4H_9)_3SnLi + 2LiCl.$

Methods a) and b) have been used successfully in other (unpublished) work on triphenyltin sodium and —lithium carried out in this laboratory.

Since this investigation was of an exploratory nature, it appeared reasonable, to begin with, to bring the tin compounds Alk_3SnM into reaction only with the most readily accessible organo-halides of other metals; in fact much of the work was carried out with compounds of the semi-metals arsenic and silicon.

Since the exploratory experiments involving the use of cacodyl chloride and trimethylchlorsilane led to anomalous and unexpected results or to unpromising mixtures of products, and there was some evidence for the partial dissociation of the alkali metal-tin compounds, the work was developed by studying the reactions of the last with the simplest reagents such as alkyl halides and carbon dioxide. These experiments confirmed the dissociation,

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li,$$

and indicated that, for example, tri-n-butyltin lithium in ether is not a good reagent to synthesize covalent bonds between tin and other metals. The reason for this conclusion is essentially that the requisite halide would normally be expected to react so quickly with n-butyl lithium (an exceedingly reactive compound) that dissociation of the tri-n-butyltin lithium would be driven towards completion. For example, reaction with trimethylchlorsilane afforded n-butyltrimethylsilane,

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li,$$

$$\underline{n}\text{-}C_4H_9Li + (CH_3)_3SiCl = \underline{n}\text{-}C_4H_9(CH_3)_3Si + LiCl,$$

instead of trimethylsilyltri-n-butyltin,

$$(\underline{n}\text{-}C_4H_9)_3SnLi + (CH_3)_3SiCl = (CH_3)_3Si\text{-}Sn(\underline{n}\text{-}C_4H_9)_3 + LiCl.$$

As there was evidence for the presence of the trialkyltin radical in the products of many of the reactions studied it was concluded that the dissociation of the tri-n-butyltin lithium was not always completed. Experiments designed in order to evaluate the use of tri-n-butyltin lithium and related compounds as synthetic reagents were then carried out, it being considered important to establish in what types of reaction they behaved as Alk_3SnLi on the one hand, and as a mixture of Alk_2Sn and Alk-Li on the other. Results from these experiments were rather inconclusive and unexpected, e.g., unpromising mixtures were produced and the reaction between tri-n-butyltin lithium and water, where the reaction between water and n-butyl lithium is extremely rapid, yielded a relatively small amount of n-butane. Thus it seemed that the reactions of trialkyltin lithium solutions in ether are even more complex than anticipated earlier.

These serious objections to the use of alkali metal derivatives of organo-tin compounds in ether having been established, attention was directed to the rather limited possibilities of using liquid ammonia as a solvent. The question of dissociation of the type just discussed does not occur in liquid ammonia, since the resulting alkali metal alkyl would react instantly with liquid ammonia and this is not observed. The results of a reaction carried out in liquid ammonia between trimethyltin sodium and dimethylgallium chloride monammine showed that reactions leading to formation of the symmetrical organo-ditin compound occurred rather than establishment of a metal to metal bond between tin and the other metal.

2. Previous Work on Alkali Metal Derivatives of Organo-Tin Compounds

Not only do organo-tin radicals of the type R_3Sn and R_2Sn take on a positive charge, thereby becoming cations, they can also take on a negative charge giving the anions R_3Sn^- and $R_2Sn^=$. They are most satisfactorily obtained by adding sodium to a liquid ammonia solution of the organotin mono- or di- halide,

$$R_3SnX + Na = R_3SnNa + NaX,$$

or by the addition of an organo-lithium compound to a suspension of stannous halide in ether,

$$3RLi + SnX_2 = R_3SnLi + 2LiX.$$

They can also be prepared by addition of alkali metal to liquid ammonia solutions of tin compounds of the types R_4Sn, R_3SnH and $R_3Sn-SnR_3$.

The alkali metal derivatives are coloured (R_2SnM_2 deep red, and R_3SnM usually yellow), and are highly reactive. They are not usually isolated since they decompose readily and are very sensitive to air and moisture, but are used immediately. Their main reactions are of the following types,

$$R_3SnM + NH_4^+ = R_3SnH + NH_3 + M^+$$

$$R_3SnM + R'X = R_3SnR' + MX$$

and

$$R_3SnM + R_3'SnX = R_3Sn-SnR'_3 + MX.$$

Trimethyltin sodium ($(CH_3)_3SnNa$) is obtained when sodium is added to a liquid ammonia solution of trimethyltin bromide,

$$(CH_3)_3SnBr + 2Na = (CH_3)_3SnNa + NaBr.$$

Evaporation of the yellow solution affords yellow crystals of the salt, which is unstable at room temperature and decomposes rapidly at higher temperatures into hydrocarbons and a tin sodium alloy.[2]

Tetramethyltin also reacts rapidly with sodium in liquid ammonia yielding trimethyltin sodium, for which the proposed reaction mechanism is:-

$$(CH_3)_4Sn + Na = (CH_3)_3Sn^{\cdot} + CH_3Na$$

$$CH_3Na + NH_3 = CH_4\uparrow + NaNH_2$$

$$(CH_3)_3Sn^{\cdot} + Na = (CH_3)_3\ddot{Sn}^{-}Na^{+}.$$

Addition of methyl iodide to a liquid ammonia solution of trimethyltin sodium immediately discharges the yellow colour of the solution with formation of tetramethyltin.

p-Dichlorobenzene reacts similarly:-

$$\underline{p}\text{-}C_6H_4Cl_2 + 2(CH_3)_3SnNa = 2NaCl + 1{:}4\ [(CH_3)_3Sn]_2C_6H_4.$$

Trimethyltin sodium also reacts with organo-tin halides. Thus hexamethyldi-tin is precipitated from liquid ammonia when trimethyltin bromide is added to trimethyltin sodium,

$$(CH_3)_3SnBr + (CH_3)_3SnNa = (CH_3)_3Sn\text{-}Sn(CH_3)_3 + NaBr.$$

This product is in fact the primary product when only one mole of sodium is added to one mole of halide,

$$(CH_3)_3SnBr + Na = (CH_3)_3Sn^{\bullet} + NaBr$$

$$2(CH_3)_3Sn^{\bullet} = (CH_3)_3Sn\text{-}Sn(CH_3)_3,$$

and can be isolated in good yield. The product reacts with more sodium[2]:-

$$(CH_3)_3Sn\text{-}Sn(CH_3)_3 + Na = (CH_3)_3Sn^{\bullet} + (CH_3)_3SnNa$$

$$(CH_3)_3Sn^{\bullet} + Na = (CH_3)_3SnNa.$$

Kraus and Greer[5] showed that addition of an ammonium salt to a solution of trimethyltin sodium in liquid ammonia caused trimethyltin hydride to separate as a heavy oil:-

$$(CH_3)_3Sn^{-} + NH_4^{+} = (CH_3)_3SnH + NH_3.$$

Triphenyltin sodium is prepared conveniently by the addition of sodium to either hexaphenylditin or triphenyltin bromide in liquid ammonia. It can be isolated as a yellow, air-sensitive powder. Kraus and Kahler[6] have shown that the product is a good conductor in liquid ammonia, being more dissociated than sodium bromate, although the limiting equivalent conductance is less. Trimethyltin sodium also conducts in liquid ammonia but has been shown to be less dissociated than triphenyltin sodium by Kraus and Johnson.[7]

Dimethyltin disodium is prepared from dimethyltin dibromide and sodium in liquid ammonia. The reaction is complex since Kraus and Greer[3] have shown that several products are formed in turn. When sodium is added to a solution of dimethyltin dibromide in liquid ammonia a yellow precipitate of polymeric dimethyltin forms initially:-

$$(CH_3)_2SnBr_2 + 2Na = [(CH_3)_2Sn]_n + 2NaBr.$$

On addition of a further gram atom of sodium the precipitate dissolves completely giving a deep red solution, which contains $[(CH_3)_2\bar{Sn}-\bar{Sn}(CH_3)_2]\ Na_2^+$ since addition of methyl iodide causes precipitation of hexamethyldi-tin:-

$$(CH_3)_2Sn + Na = (CH_3)_2Sn^{-\cdot} + Na^+$$

$$2(CH_3)_2Sn^{-\cdot} = (CH_3)_2\bar{Sn}-\bar{Sn}(CH_3)_2$$

$$(CH_3)_2\bar{Sn}-\bar{Sn}\ (CH_3)_2 + 2CH_3I = (CH_3)_3Sn-Sn(CH_3)_3 + 2I^-.$$

Addition of more sodium gives a very deep red solution. When one more gram atom of sodium has been added per gram atom of tin the solution contains $(CH_3)_2SnNa_2$ since addition of methyl iodide results in formation of tetramethyltin:-

$$(CH_3)_2\bar{S}n-\bar{S}n(CH_3)_2 + 2Na = (CH_3)_2Sn^{=} + 2Na^{+}$$

$$(CH_3)_2Sn^{=} + 2CH_3I = (CH_3)_4Sn + 2I^{-}.$$

Dimethyltin disodium has proved useful for preparation of compounds containing chains of tin atoms.

Gilman and Rosenberg[1] have reported that triethyltin lithium ($((C_2H_5)_3SnLi)$) is formed in a reaction in which ethyl lithium is added to a suspension of stannous chloride in ether at -10°. When two moles of ethyl-lithium have been added, the solution is deep red, and does not contain any ethyl lithium but diethyltin, which then reacts with more ethyl lithium:-

$$2C_2H_5Li + SnCl_2 = (C_2H_5)_2Sn + 2LiCl$$

$$(C_2H_5)_2Sn + C_2H_5Li = (C_2H_5)_3SnLi$$

Addition of ethyl bromide discharges the deep red colour of the solution with formation of tetraethyltin. Solutions said to contain triphenyltin lithium and tri-n-butyltin lithium have also been prepared similarly.[8,1]

Compounds containing tin-tin bonds have been prepared by reactions between organo-tin alkali compounds and organo-tin halides. Kraus and Bullard[9] have reported that the compound $(CH_3)_3SnSn(C_2H_5)_3$ is formed when tri-methyltin sodium reacts with triethyltin bromide in liquid ammonia.

Triphenyltrimethyldi-tin was prepared by Kraus and

Bullard[9] from triphenyltin sodium and trimethyltin bromide in liquid ammonia. The reverse reaction between trimethyltin sodium and triphenyltin bromide led to a mixture of products consisting of hexamethyldi-tin, triphenyltrimethyldi-tin and hexaphenyldi-tin.

The compound diethylhexamethyltri-tin was prepared by Kraus and Greer[3] by the following reactions:-

$$2(CH_3)_2SnNa_2 + (CH_3)_2SnBr_2 = Na(CH_3)_2Sn-(CH_3)_2Sn-Sn(CH_3)_2Na + 2NaBr$$

$$Na(CH_3)_2Sn-(CH_3)_2Sn-Sn(CH_3)_2Na + 2C_2H_5Br = 2NaBr + (CH_3)_2C_2H_5Sn-(CH_3)_2Sn-SnC_2H_5(CH_3)_2$$

A compound analogous to fully methylated n-butane has also been prepared by Kraus and Neal,[4] and Kraus and Greer[3] have reported a compound analogous to n-pentane. These compounds are viscous liquids, which quickly absorb oxygen.

3. Experimental

(a) Drying and Purification of Solvents in General Use

Ether

Magnesium (24.3 gms., 1 mole) was stirred with dry ether (approximately 100 c.c.'s) in a 5-litre three-necked flask fitted with a dropping funnel, reflux condenser, and a stirrer fitted with a nitrogen inlet. Some of the magnesium was activated by heating with a few crystals of iodine. The apparatus was filled with nitrogen and a solution of bromobenzene (140 gms., 0.9 mole) in dry ether (200 c.c.'s) was added slowly. When reaction began the stirrer was started and the rest of the bromobenzene solution was added at such a rate that the ether refluxed gently. The amounts of magnesium and bromobenzene were such that the magnesium was in excess thus ensuring complete reaction with the bromobenzene. Commercial ether, distilled from sodium, was then added until the volume of solution was approximately three litres. Dry ether was then distilled from the Grignard solution into receivers and stored over sodium wire. The presence of Grignard reagent was shown by removing samples of solution by pipette and adding to a solution of Michler's ketone (tetramethyldiaminobenzophenone) in dry benzene. The solution was then hydrolysed by the addition of water and then a few drops of 0.2% iodine in glacial acetic acid were added. The development of an intense greenish-blue colour indicated the presence of Grignard reagent.[10] Generally it was possible to add more ether to the 5-litre flask, after the first distillation, before all the Grignard reagent was exhausted.

At later stages ether was also dried much more conveniently by standing the ether over sodium wire. When evolution of gases ceased the ether was ready for use.

Tetrahydrofuran

About three litres of tetrahydrofuran were stirred in a 5-litre three-necked flask with a small amount of potassium under nitrogen. The solution was refluxed gently, heat being supplied from an isomantle. After one hours refluxing a small quantity of benzophenone was added. The development of a blue colour indicated the absence of water. The dried tetrahydrofuran was then distilled off and collected in a receiver over sodium wire. An adaptor was fitted to the receiver so that the solvent was blown out of the flask by the application of a pressure of nitrogen. In this way contamination of the solvent by moisture was kept to a minimum.

Benzene

Benzene (of low sulphur content and high purity) was dried in exactly the same way as that used for tetrahydrofuran. The dried distilled benzene was stored over sodium wire as in the previous case. The adaptor fitted to the flask was arranged so that benzene was removed by blowing dry air into the flask.

Methyl Alcohol

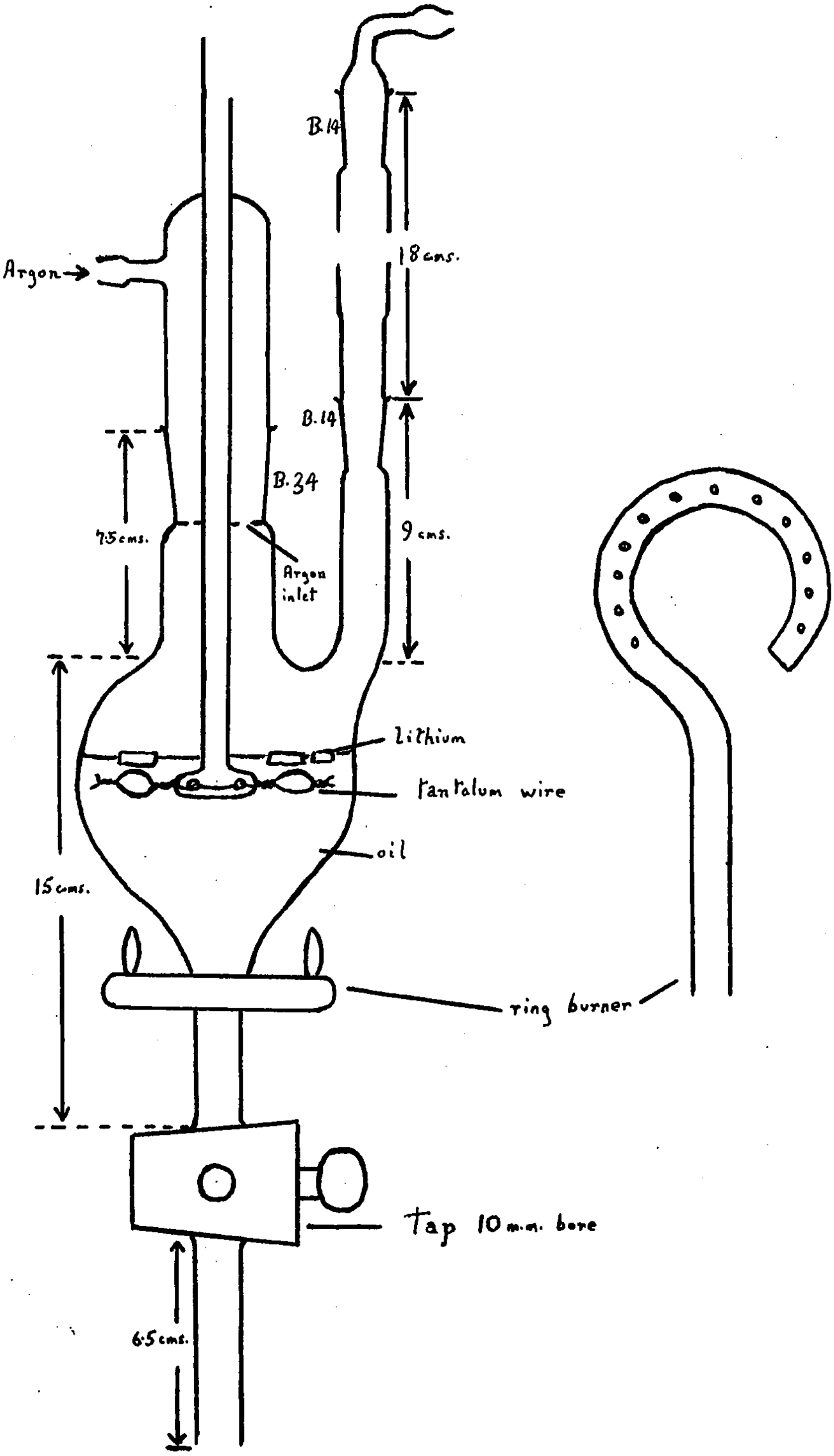
Magnesium (24.3 gms., 1 mole) was placed in a 2-litre flask fitted with a stirrer, dropping funnel, and a reflux condenser. A drying tube filled with anhydrous calcium sulphate was fitted to the condenser. About 200 c.c.'s of methyl alcohol (dried previously by this method) was added slowly to the magnesium with stirring. When reaction (formation of magnesium methoxide) had nearly ceased about one litre of methyl alcohol, dried over anhydrous magnesium sulphate, was added. Dried methyl alcohol was then distilled from the flask. The alcohol was stored in a receiver fitted with a silicone-greased stopper.

(b) Preparation of Lithium Shot

In heterogeneous reactions between an organic halide, usually in an organic solvent, and metallic lithium it is advantageous to have the lithium in a fine form with a large clean surface area. This was achieved as follows.

Lithium, cut into suitable squares, was placed in a 250 c.c. two-necked flask fitted with a stirrer with an argon inlet, and a short air-condenser. A tap of large bore (10 m.m.'s) was fitted to the bottom of the flask. Petroleum oil, olefin free, b.pt. 210-230°C. was added to cover

APPARATUS FOR PREPARATION OF LITHIUM PELLETS



the stirrer, which was made of stainless steel or tantalum wire. (Unsaturated products had been removed from the oil by treatment with concentrated sulphuric acid followed by acid permanganate; the oil was then washed with water and finally distilled). Two or three drops of oleic acid were then added to the oil (to prevent coalescing of the lithium). The apparatus was flushed out with argon and then heated by means of a small ring gas burner, maintaining a slow flow of argon through the apparatus. The lithium being less dense than the oil floated on the surface. When the lithium melted heating was discontinued and the stirrer speed was increased in order to break up the lithium. After the lithium was broken up stirring was maintained at such a rate as to prevent coalescing of the pellets formed. When the oil was cooled well below 186°C. (m.pt. of lithium) stirring was stopped leaving clean pellets of lithium floating on the oil, while impurities settled to the bottom of the flask. The excess oil and impurities were then drawn off from the bottom of the apparatus. Generally the lithium shot stuck to the sides of the vessel so that it was possible to recover almost all the oil. The lithium shot was then washed with the solvent to be used in the reaction, *e.g.*, ether tetrahydrofuran *etc.*, and then the solvent was drained off as before. The washing process was repeated and finally the lithium shot was washed through the tap at the bottom of

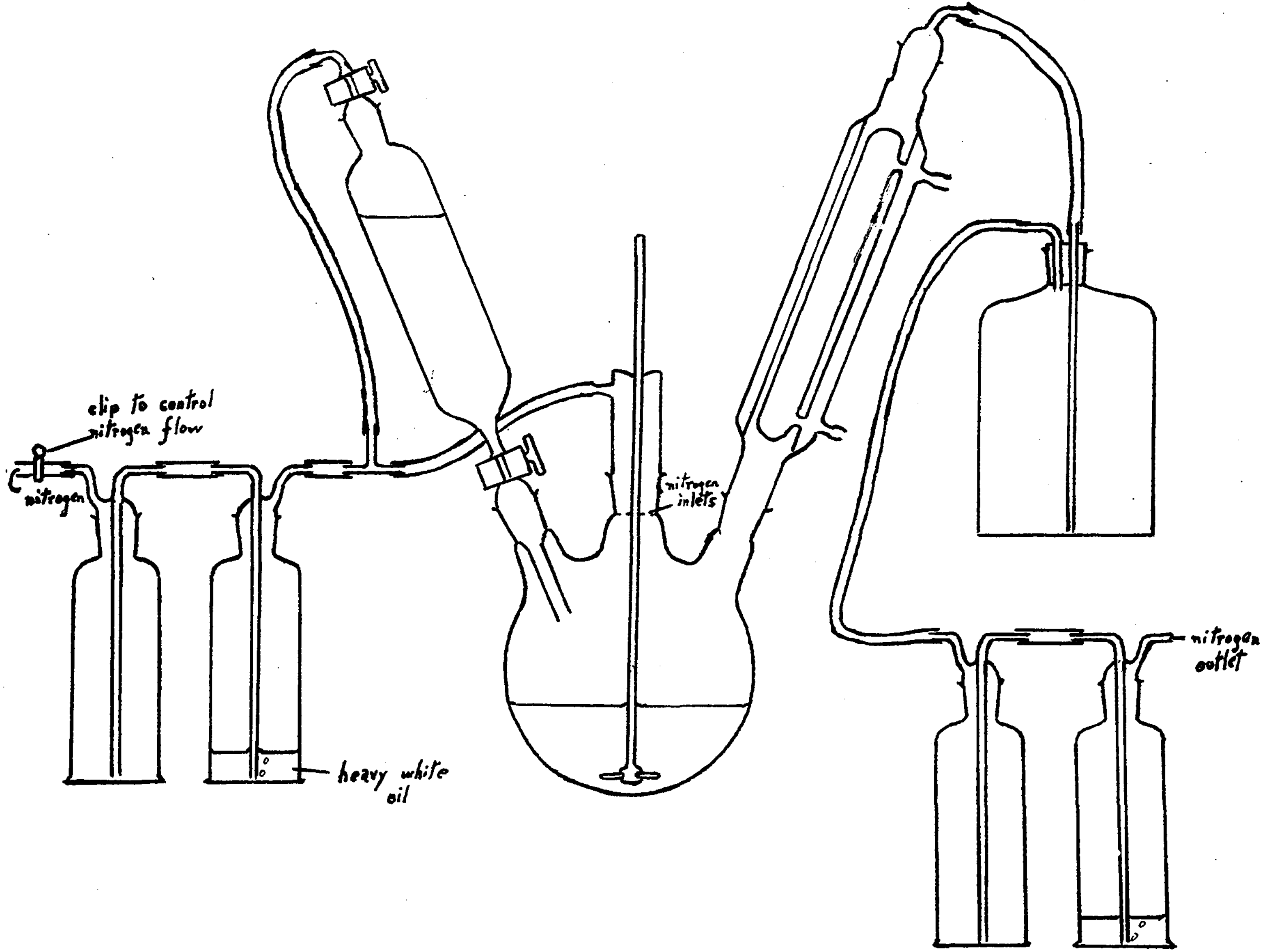

clip to control nitrogen flow
nitrogen
heavy white oil
nitrogen inlets
nitrogen outlet

Fig. 1

the apparatus into the reaction vessel, against a counter current of nitrogen.

Nitrogen could not be used when the lithium was heated because of the danger of formation of lithium nitride. However, for reactions at room temperature and slightly above, the rate of formation of nitride is slow and so it is permissible to use oxygen-free nitrogen.

(c) Manipulation of and Apparatus Used in Reactions with Air-Sensitive Compounds

As the major part of this research involved the use of air-sensitive compounds it was necessary to develop various techniques and types of apparatus in order to handle such compounds. Commercial oxygen-free nitrogen from cylinders, dried by passage through potassium hydroxide pellets, was used to maintain an inert atmosphere in the reaction vessels (only in the preparation of lithium shot was another atmosphere required *pp*. 13).

a). General Reaction Assembly and Method of Maintaining an Inert Atmosphere

The diagram (Fig. 1) shows a general reaction assembly for preparation of an air-sensitive compound. Before reaction was started a rapid stream of oxygen-free nitrogen was passed through the apparatus to remove air (*ca*. 3 mins.), the nitrogen being led in *via* the stirrer; after this stage only a slow stream of nitrogen was maintained. The winchester served two purposes, one to increase the capacity

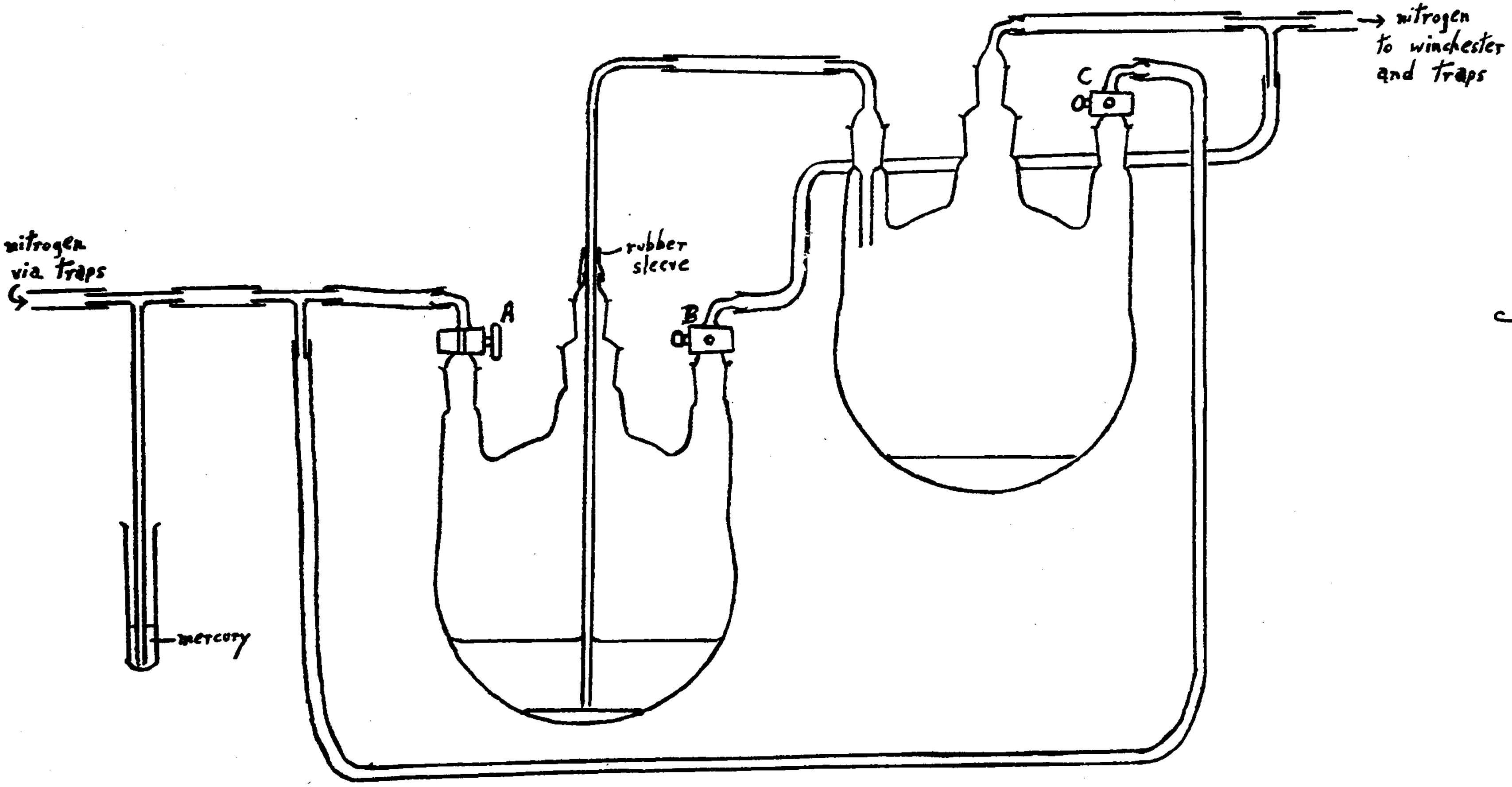

nitrogen via traps
mercury
A
rubber sleeve
B
C
nitrogen to winchester and traps

Fig. 2

of the system and thus reduce fluctuations due to pressure changes in the system, and secondly in the event of air being sucked into the system to dilute it considerably with a large volume of nitrogen. The traps were made from Drechsel wash-bottles arranged in pairs as shown, one of which contained heavy white oil, thus, in the event of any suck-back, oil was only displaced into the empty Drechsel and not any other part of the apparatus. A side-tube was attached to the top of the dropping funnel to serve as a pressure equaliser.

When the reaction vessel was heated, and then allowed to cool on completion of the reaction, it was necessary to increase the flow of nitrogen into the system during cooling to prevent air being drawn into the system. This also applied when the reaction vessel was cooled prior to reactions carried out below room temperature.

b). <u>Transference of Air-Sensitive Solutions</u>

i). When large volumes of solution ($>$ 1 litre) were transferred under nitrogen the apparatus used was arranged as shown in Fig. 2. Both flasks were fitted with nitrogen gas inlets and outlets connected to the same trap system. The connecting tubing between the flasks was either of rubber or polythene. The empty flask was purged with nitrogen before connection to the other flask. A rapid stream of nitrogen was passed through both systems while connection was being made

Fig. 3

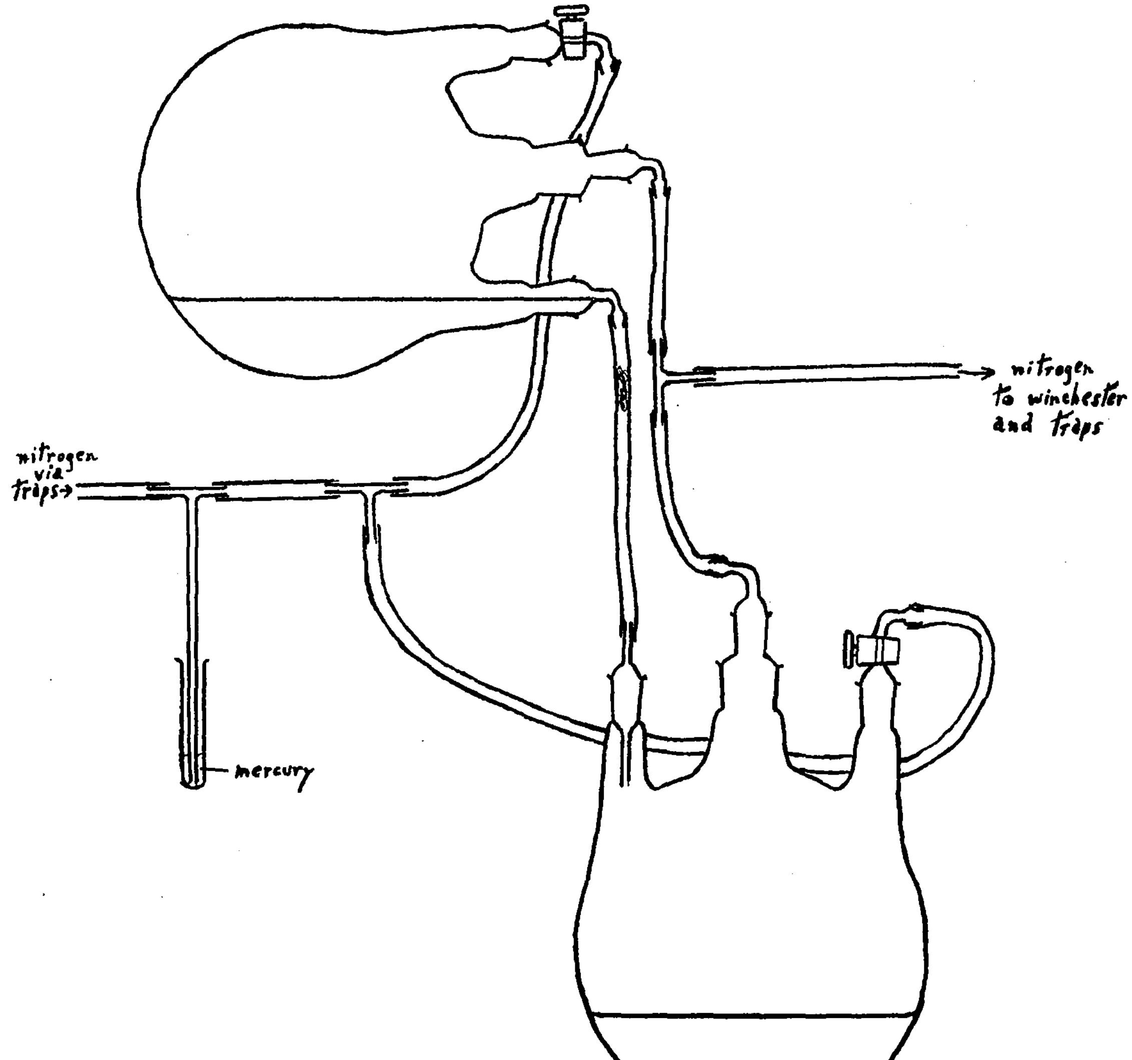
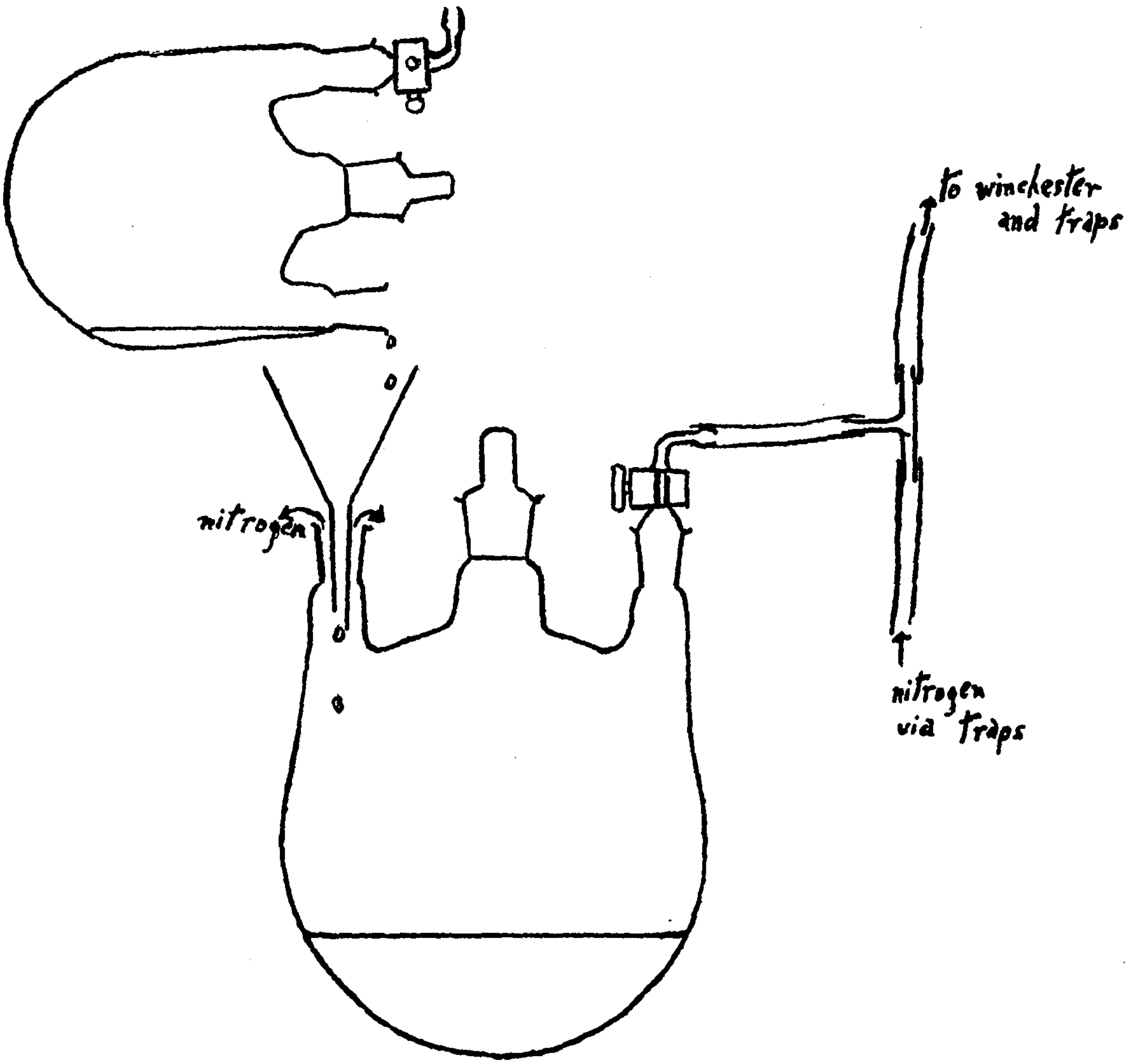

nitrogen to winchester and traps
nitrogen via traps
mercury

Fig. 4



to prevent entry of air, after which the flow of nitrogen was kept to a minimum. To force liquid into the empty flask taps B and C were closed with A left open. As the pressure in the first flask was above atmospheric the adaptors on this flask were clamped securely. A mercury sealed T-piece prevented too large a pressure developing in the system. The rubber sleeve fitted to the long lead in the first flask allowed it to be adjusted to fit flasks of varying capacities. The opening of either tap B or C stopped transference of liquid to the second flask immediately, by equalizing the pressure in both flasks.

ii). Smaller amounts of air-sensitive solution (ca. 500 c.c.) were transferred to other flasks by decantation under nitrogen. The apparatus used was practically the same as that described previously. The liquid was poured through the connecting polythene or rubber tubing into the other flask (Fig. 3). If solid impurities were present in the liquid a loose glass-wool plug in the connecting tubing proved advantageous in keeping back large amounts of the solid while allowing transference of the liquid.

iii). If the liquid to be transferred was not particularly air-sensitive it was often possible to pour the liquid rapidly from one flask to the other against a vigorous counter current of nitrogen (Fig. 4). The stoppering of the receiver caused the nitrogen stream to be

Fig. 5

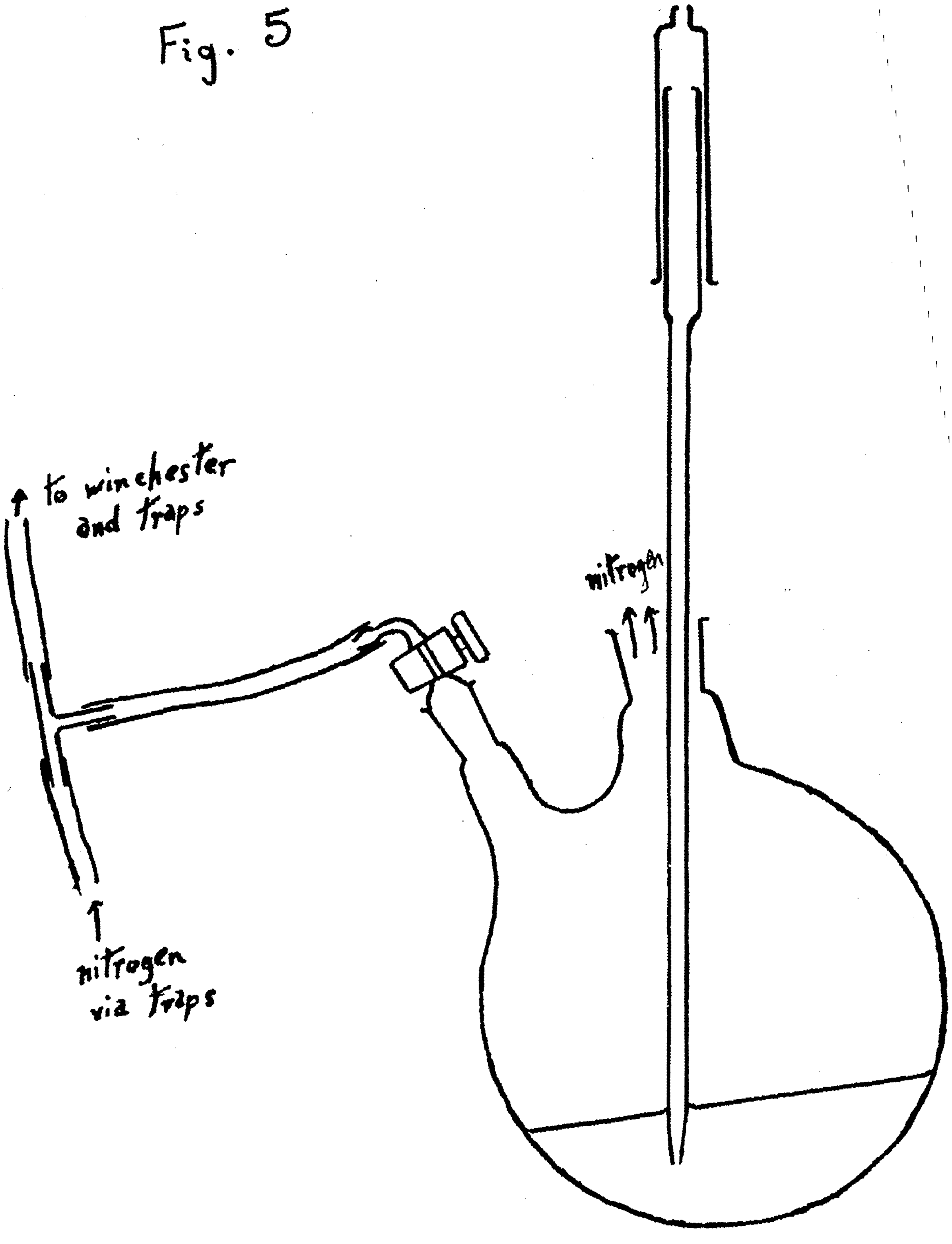
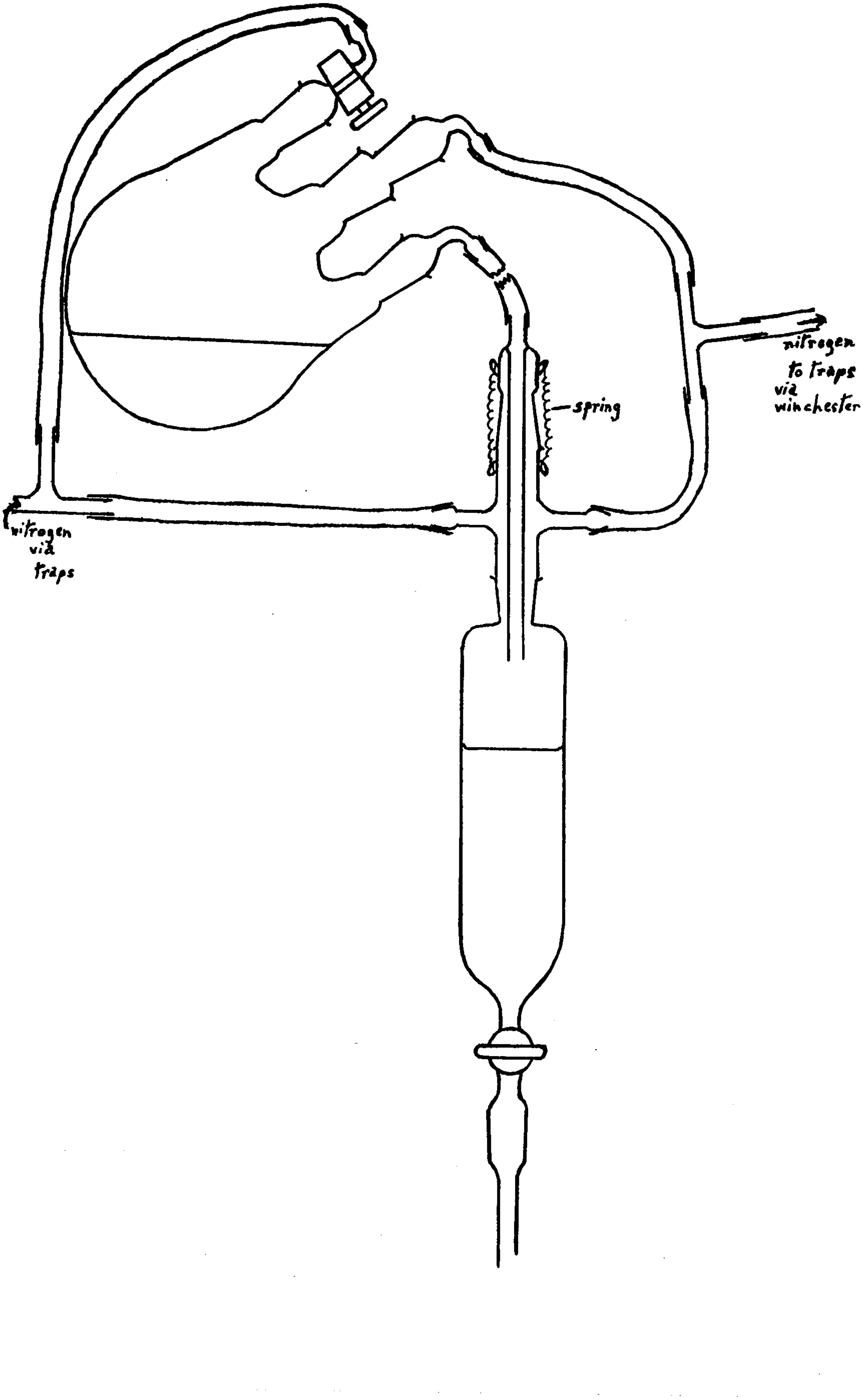


Fig. 6


nitrogen to traps via winchester
spring
nitrogen via traps

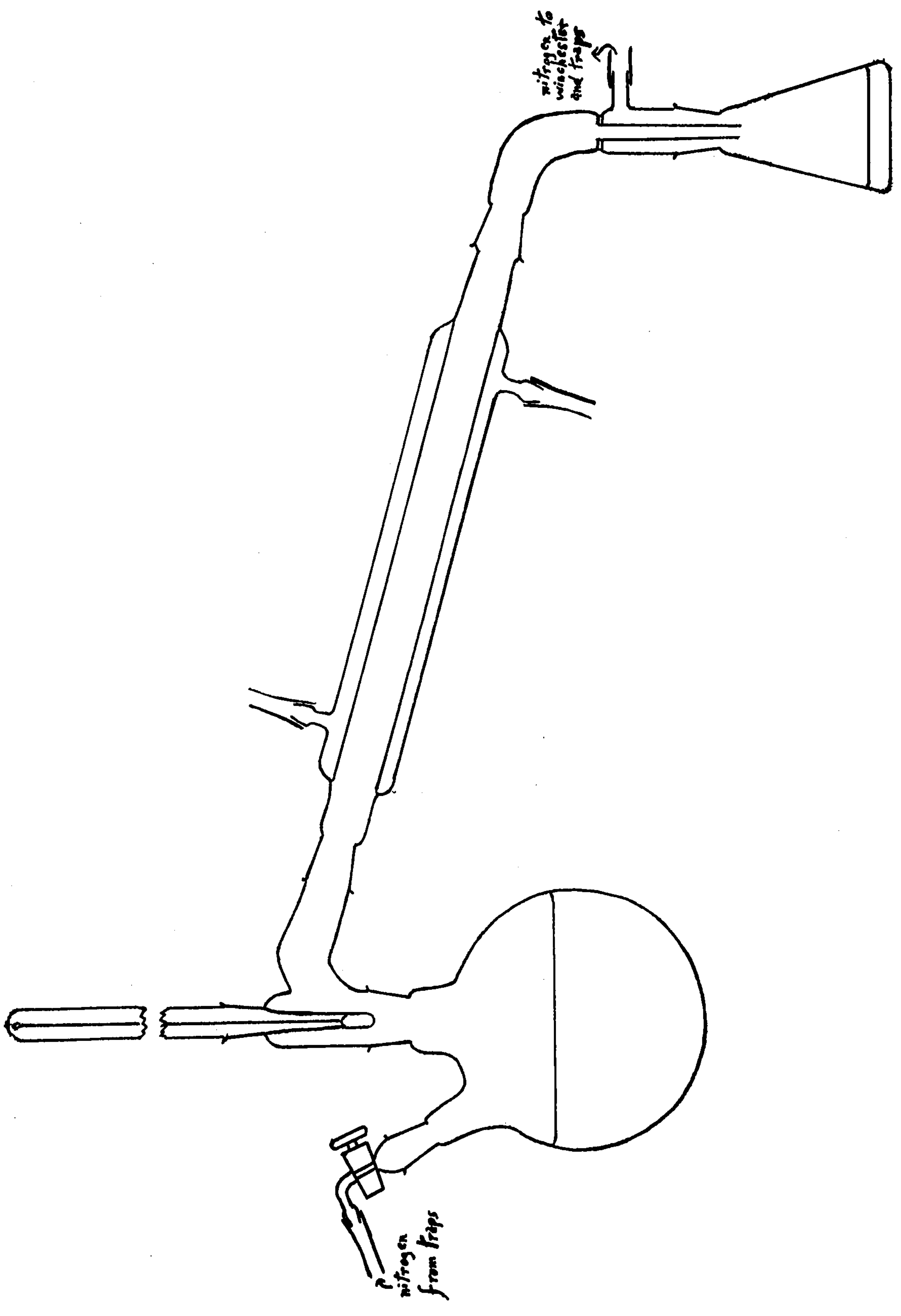
diverted through the trap system thus preventing any development of excess pressure in the receiver.

c). Measurement of Air-Sensitive Solutions

i). Small amounts of liquid (ca. 10 c.c.) were measured by means of graduated Excelo pipettes (Fig. 5). Immediately before use the pipette was purged out with nitrogen and then placed in the flask against a counter current of nitrogen. The required volume of solution was then drawn into the pipette, which was then withdrawn quickly and the liquid ejected into the other flask against a counter current of nitrogen. In this way it was possible to measure out small volumes of inflammable materials such as cacodyl and tri-ethylphosphine. The diagram also illustrates the method of storing air-sensitive compounds in stoppered two-necked flasks fitted with a gas lead, which was closed by means of a tap. When required the gas lead on the flask was connected to a suitable nitrogen supply.

ii). Large volumes of air-sensitive liquids or solutions were measured in graduated dropping funnels by decantation under nitrogen (Fig. 6). The flask and dropping funnel were fitted with nitrogen inlets and outlets so that the whole system was maintained at the same pressure. The dropping funnel which usually contained air initially, was purged out by passing nitrogen through it with the tap of the dropping funnel open and then closing the tap when the

Fig. 7

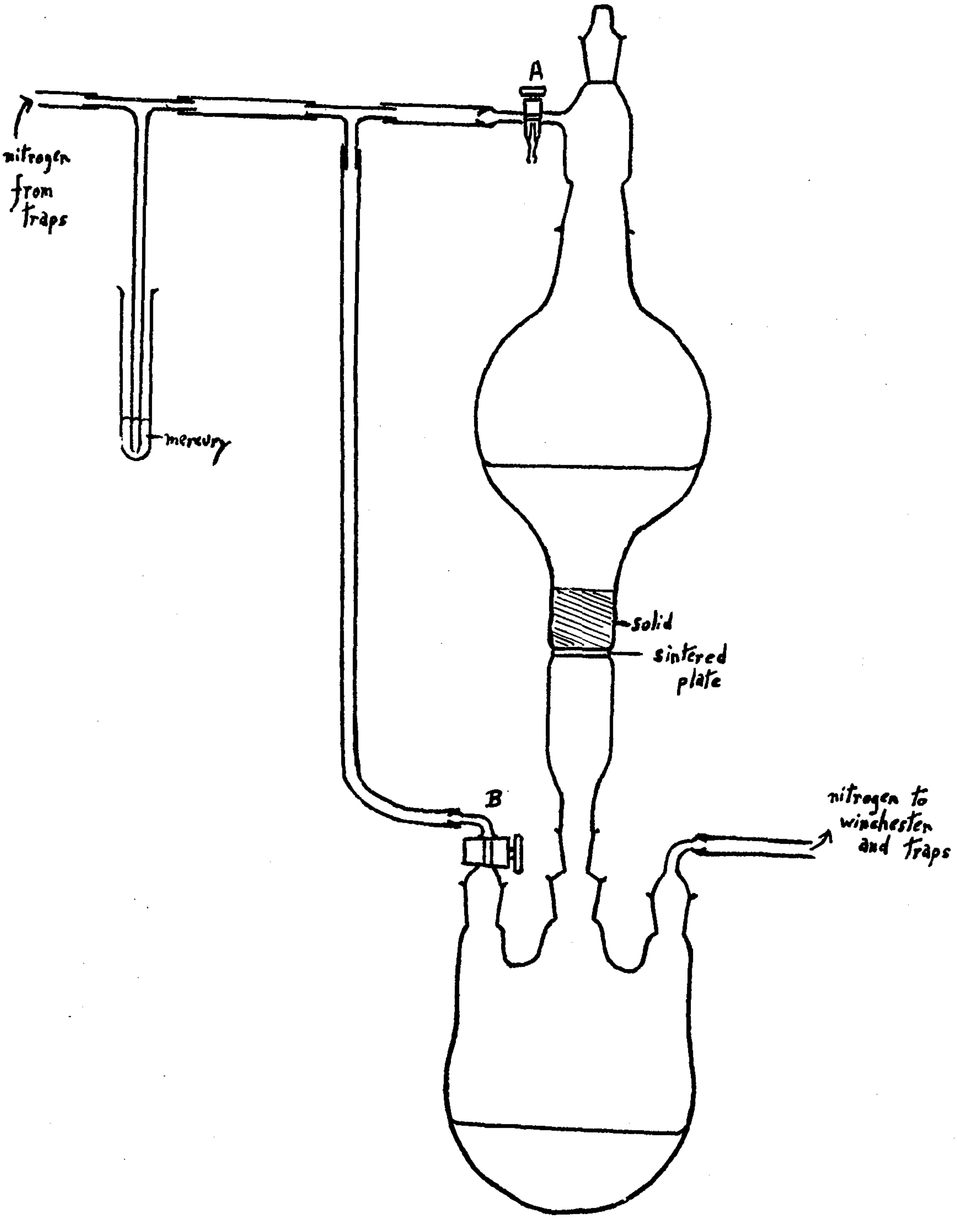


air had been expelled. The connecting tubing and adaptor, usually joined only to the dropping funnel initially, was also purged with nitrogen and the adaptor on the end of the tubing stoppered with a rubber bung until required. When required the rubber bung was removed in a vigorous stream of nitrogen and quickly joined to the flask through which a vigorous stream of nitrogen also passed. The flow of nitrogen was then kept to a minimum. When the desired quantity of liquid had been transferred to the dropping funnel the inlet tube to it was replaced by a cap. The dropping funnel was then connected to the reaction vessel, the nitrogen inlets and outlets being connected as before to maintain an equal pressure in the whole system. The dropping funnel was then used in the normal way.

d). Distillations under Nitrogen

The apparatus used for distillation of an air-sensitive compound, or removal of solvent from such a compound, was essentially that used in ordinary circumstances with the addition of a nitrogen inlet and outlet (Fig. 7). As the liquid was air-sensitive pieces of porous pot were not generally used. If the flask was heated up slowly distillation generally proceeded without violent bumping. The apparatus, except the flask, was assembled first and then the flask was connected to the system with a rapid stream of nitrogen passing through it. After the apparatus had been purged with nitrogen

Fig. 8

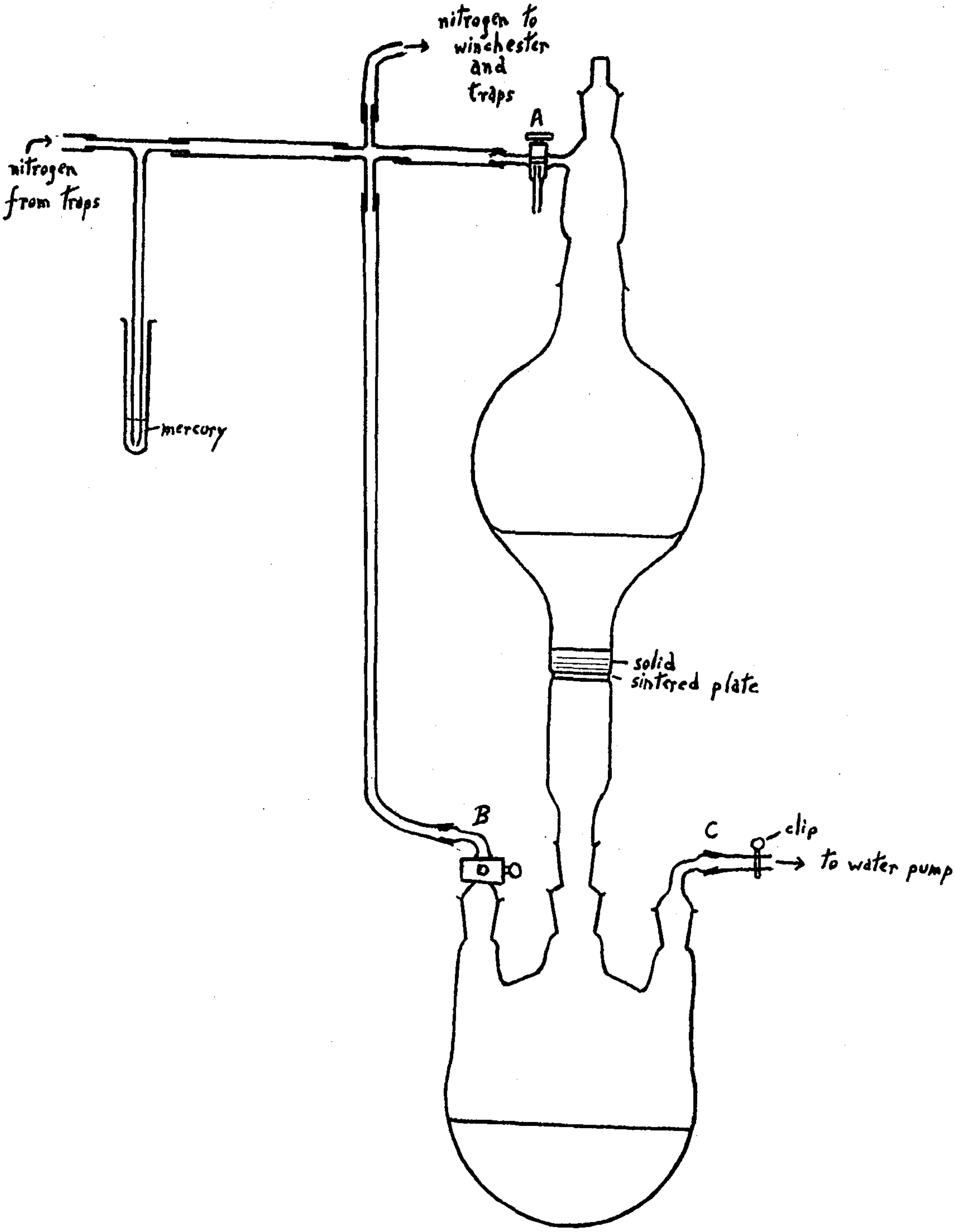

A
nitrogen from traps
mercury
solid
sintered plate
B
nitrogen to winchester and traps

the flow was cut down to a minimum. Distillation was then carried out in the normal way. The apparatus could also be adapted for distillations under reduced pressure. In this case the receiver was connected by pressure tubing, via two traps cooled in liquid nitrogen, to an oil pump. Either the apparatus, under nitrogen, was pumped down slowly to the required pressure, in order to prevent bumping, isolated from the pump, and the liquid distilled, or a leak connected to the nitrogen supply was used with continuous pumping. In both cases when distillation was completed the apparatus was refilled with nitrogen to atmospheric pressure.

e). Filtration of Air-Sensitive Solutions

The apparatus described here was used to separate air-sensitive liquids from solid impurities. The liquid/solid mixture was transferred to the apparatus (Fig. 8) in one of the ways described previously, the apparatus being filled with nitrogen in the usual way. If filtration was slow under gravity pressure was applied by closing tap B, the mercury sealed T-piece being used to prevent too large a pressure being applied. In this case the apparatus was clamped securely to prevent joints being broken due to the applied pressure of nitrogen. The rate of filtration could also be increased by reducing the pressure in the flask below the sintered plate (Fig. 9). Tap B was closed and clip C, on the tubing

Fig. 9

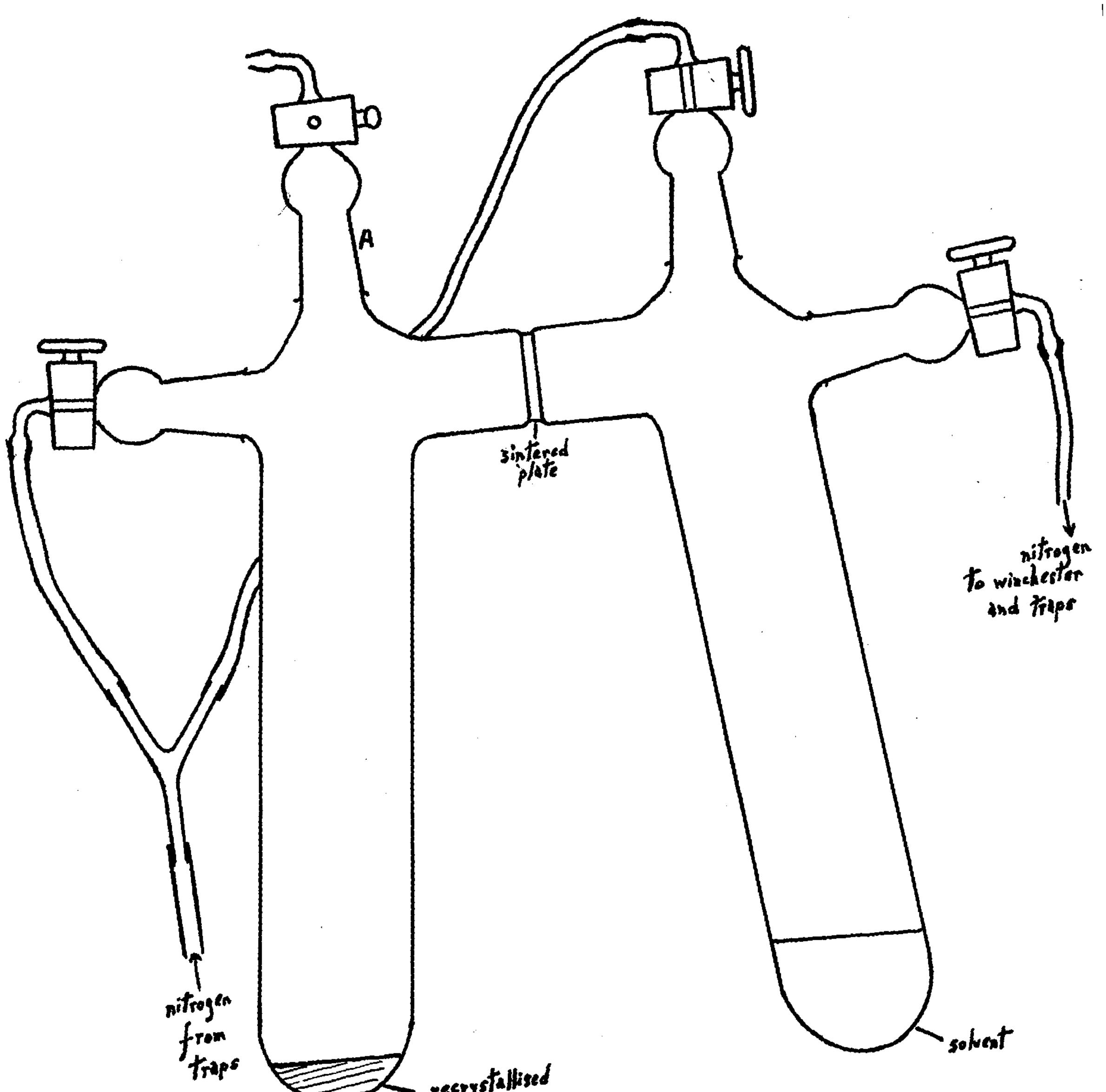

nitrogen to winchester and traps
A
nitrogen from traps
mercury
solid
sintered plate
B
C
clip
to water pump

leading to a water pump, was opened occasionally to reduce the pressure in the flask.

f). Recrystallisation of Air-Sensitive Solids

The apparatus used to recrystallise air-sensitive solids consisted of a modified double Schlenk tube (Fig. 10). The solid was placed in one limb of the apparatus, which was filled with nitrogen. A suitable solvent was added through one of the standard joints (A) by means of a fitted dropping funnel. The solid was then recrystallised from the solvent, which was heated by a water bath placed around the limb, or the solid was frozen out from a saturated solution at room temperature. The latter method was used to recrystallise substances which were thermally unstable. Solvent was removed by tilting the apparatus and allowing the liquid to run into the other limb *via* the sintered plate, which held back recrystallised material. If this was done carefully the bulk of recrystallised material could be left in the bottom of the limb, *e.g.*, small amounts of material were usually collected on the sintered plate and walls of the limb when the apparatus was tilted. The solvent, if volatile, could be re-used; the apparatus was evacuated by means of a water pump and solvent condensed onto the solid by cooling the limb with a solid carbon dioxide/acetone bath. Recrystallisation was then carried out as before. Finally the purified solid was freed from traces of solvent by pumping *in vacuo*; this also removed the solvent collected in

Fig. 10


A
sintered plate
nitrogen to winchester and traps
nitrogen from traps
recrystallised solid
solvent

the other limb.

(d) Reactions in Tetrahydrofuran with Trimethyltin Bromide

Preparation of Tetramethyltin[11]

$$4CH_3MgI + SnCl_4 = (CH_3)_4Sn + 2MgI_2 + 2MgCl_2.$$

Di-n-butyl ether was dried and purified by refluxing with sodium under nitrogen and then distilling off the ether.

Magnesium (200 gms., 8.2 moles), some of which was warmed with a few crystals of iodine, was stirred in a three-necked flask (5 litres capacity) with ~ 2½ litres of dry di-n-butyl ether. Dry oxygen-free nitrogen was led into the flask *via* the stirrer. Methyl iodide (400 c.c.'s., 6.4 moles) was slowly added. When reaction had started the flask was cooled in a large tub of water, and the rest of the methyl iodide added over a period of two hours. The reaction mixture remained at ~ 30°-40°C. during addition but was allowed to warm to 50°-60°C. towards the end to ensure that all the methyl iodide was used up. The reaction mixture was then cooled in cold water to which some ice was added, and stannic chloride (redistilled, 162 c.c.'s, 360 gms., 1.38 moles) was added over a period of one hour; during the addition the temperature was maintained at ~ 30°-40°C. When the addition had been completed the cooling bath was removed and replaced by an isomantle and the reaction mixture was refluxed for one hour. The reaction mixture was then distilled, and liquid boiling up to 135°C. was collected ($\sim$1,000 c.c.'s). Fractionation gave tetramethyltin (100 gms., 0.55 mole, 40% yield), b.pt. 77.5-78°C.

In another preparation methyl magnesium iodide was prepared from magnesium (150 gms., 6.15 moles) and methyl iodide (350 c.c.'s, 5.6 moles) in $\sim 2\frac{1}{2}$ litres of di-*n*-butyl ether. A mixture of stannic bromide (454 gms., 1.03 moles) and stannic chloride (44 gms., 0.17 mole), liquid at room temperature was used in this case instead of stannic chloride. The magnesium bromide formed on reaction with the methyl magnesium iodide was more soluble in the ether than magnesium chloride (when stannic chloride was used) thus making the stirring of the reaction mixture easier. After working up, tetramethyltin (162 gms., 0.91 mole, 76% yield) b.pt. 77.5-78.5°C. was obtained.

Preparation of Trimethyltin Bromide[2]

$$(CH_3)_4Sn + Br_2 = (CH_3)_3SnBr + CH_3Br$$

Tetramethyltin (257.5 gms., 1.44 moles) was stirred in a 500 c.c. three-necked flask fitted with a stirrer, reflux condenser and dropping funnel. The flask was cooled by means of an ice-bath. Bromine (230.5 gms., 1.44 moles) was dropped slowly into the stirred reaction mixture over three hours. After the reaction mixture had warmed up to room temperature it was distilled through a short vacuum-jacketed column, a fraction of trimethyltin bromide (290 gms., 1.19 moles 83% yield) b.pt. 163-165°C. was collected (Literature[2]:- b.pt. 165°C., m.pt. 27°C.). Further purification was effected by melting the product, allowing the bulk of liquid to recrystallise and pouring off the residual liquid. Trimethyltin bromide (252 gms., 1.04 moles 72% yield) m.pt. 27°C. was obtained.

Attempted Preparation of Trimethyltin Lithium from Trimethyltin Bromide and Lithium in Tetrahydrofuran

$$(CH_3)_3SnBr + 2Li = (CH_3)_3SnLi + LiBr.$$

Reactions between trimethyltin bromide and lithium were carried out under oxygen-free nitrogen as compounds of the type R_3SnLi were expected to be both oxygen and moisture sensitive.

When trimethyltin bromide (12.2 gms., .05 mole) in dry tetrahydrofuran (40 c.c.'s) was added to a stirred suspension of lithium shot (1 gm., 0.15 mole) in tetrahydrofuran (60 c.c.'s) some heat was generated and the solution became yellowish-green in colour. When addition was completed stirring was continued for another 15 minutes.

The yield of trimethyltin lithium was estimated by removing 2 c.c. aliquots, by pipette, and hydrolysing them in turn with wet ether, alcohol and then water. This provided a means of smooth hydrolysis:-

$$(CH_3)_3SnLi + H_2O = (CH_3)_3SnH + LiOH.$$

The alkali was then determined by titration with 1N hydrochloric acid using methyl red as indicator. Although trimethyltin hydride does react with concentrated hydrochloric acid,[5]

$$(CH_3)_3SnH + HCl \quad = \quad (CH_3)_3SnCl + H_2,$$

it was thought that in dilute solution, especially where the solution remained alkaline until all lithium hydroxide had been titrated, and where only normal hydrochloric acid was used this reaction would be slow. The result obtained in this case indicated a yield of 124% of trimethyltin bromide which was thought to be due to the removal of excess lithium as well as solution by pipette, and not due to reaction of trimethyltin hydride with the acid.

Reaction with Trimethylchlorosilane

$$(CH_3)_3SnLi + (CH_3)_3SiCl \quad = \quad (CH_3)_3Sn\text{-}Si(CH_3)_3 + LiCl.$$

Trimethylchlorsilane (5.4 gms., .05 mole) equivalent to 100% yield of trimethyltin lithium was slowly added, in tetrahydrofuran (40 c.c.'s) with stirring, to the trimethyltin lithium solution prepared as just described. The yellowish-green colour disappeared on addition of the silane. Then the solution was blown through rubber tubing, containing a glass-wool plug to keep back excess lithium, into a flask flushed out with nitrogen.

The reaction mixture was then distilled under nitrogen.

A fraction, b.pt. 65°-90°C, was collected when the bulk of solvent (b.pt. 65°C.) had been removed. The residue in the flask, mainly solid, was evacuated to .03 m.m.'s., and heated, all volatile liquid being collected in a trap cooled in liquid nitrogen. This amount was very small. The fraction collected previously was then distilled through a short vacuum-jacketed column, without exclusion of air. The desired product $(CH_3)_3Sn\text{-}Si(CH_3)_3$ was not expected to be particularly oxygen-sensitive. Only a very small amount of liquid was collected after removal of more solvent; no higher fraction was observed although the flask was heated to ~190°C. A fraction of liquid b.pt. 112°C. was collected (hexamethyldisilane, b.pt. 112°C.). The observed boiling point suggested that reactions of the type shown below might occur:-

$$(CH_3)_3SiCl + (CH_3)_3SnLi = (CH_3)_3SiLi + (CH_3)_3SnCl,$$

$$(CH_3)_3SiLi + (CH_3)_3SiCl = (CH_3)_3Si\text{-}Si(CH_3)_3 + LiCl.$$

This reaction was not proceeded with as very little volatile product had been obtained other than solvent. The product $(CH_3)_3SnSi(CH_3)_3$ was expected to be a liquid boiling about 160°C.

Reaction with Triphenyltin Bromide

The reaction between trimethyltin bromide and lithium was carried out as in the previous preparation. In this case, however, the solution was blown through a rubber tube containing a glass-wool plug into a graduated dropping funnel. This served to obtain an accurate known volume of solution and to remove excess lithium particles. From the volume of solution and titration of aliquots, as described, the yield of trimethyltin lithium, calculated from alkali generated on hydrolysis, was estimated (86%). This solution was then run into a calculated quantity of triphenyltin bromide (18.5 gms., .043 mole) in tetrahydrofuran (40 c.c.'s) under nitrogen. The greenish-yellow colour of the trimethyltin lithium solution disappeared leaving a colourless solution. After this stage working up was carried out without exclusion of air as the expected product $(C_6H_5)_3SnSn(CH_3)_3$ was not oxygen sensitive. From the concentrated tetrahydrofuran solution diluted considerably with water there was obtained insoluble material. This was extracted with <u>cyclo</u>-hexane when 7.5 gms. of solid dissolved. This was recovered and after recrystallisation from benzene the melting point was found to be 231°C. This indicated formation of hexaphenylditin (m.pt. 232°C.), and represented 51.4% recovery of the tin from the triphenyltin bromide used.

As the total recovery of tin was small the aqueous phase was extracted to remove any matter soluble in ether (such as organotin halides). However, no solid or liquid was extracted. There was no indication of the formation of

$(C_6H_5)_3SnSn(CH_3)_3$ (m.pt. 106°C.), nor could the loss of tin be accounted for.

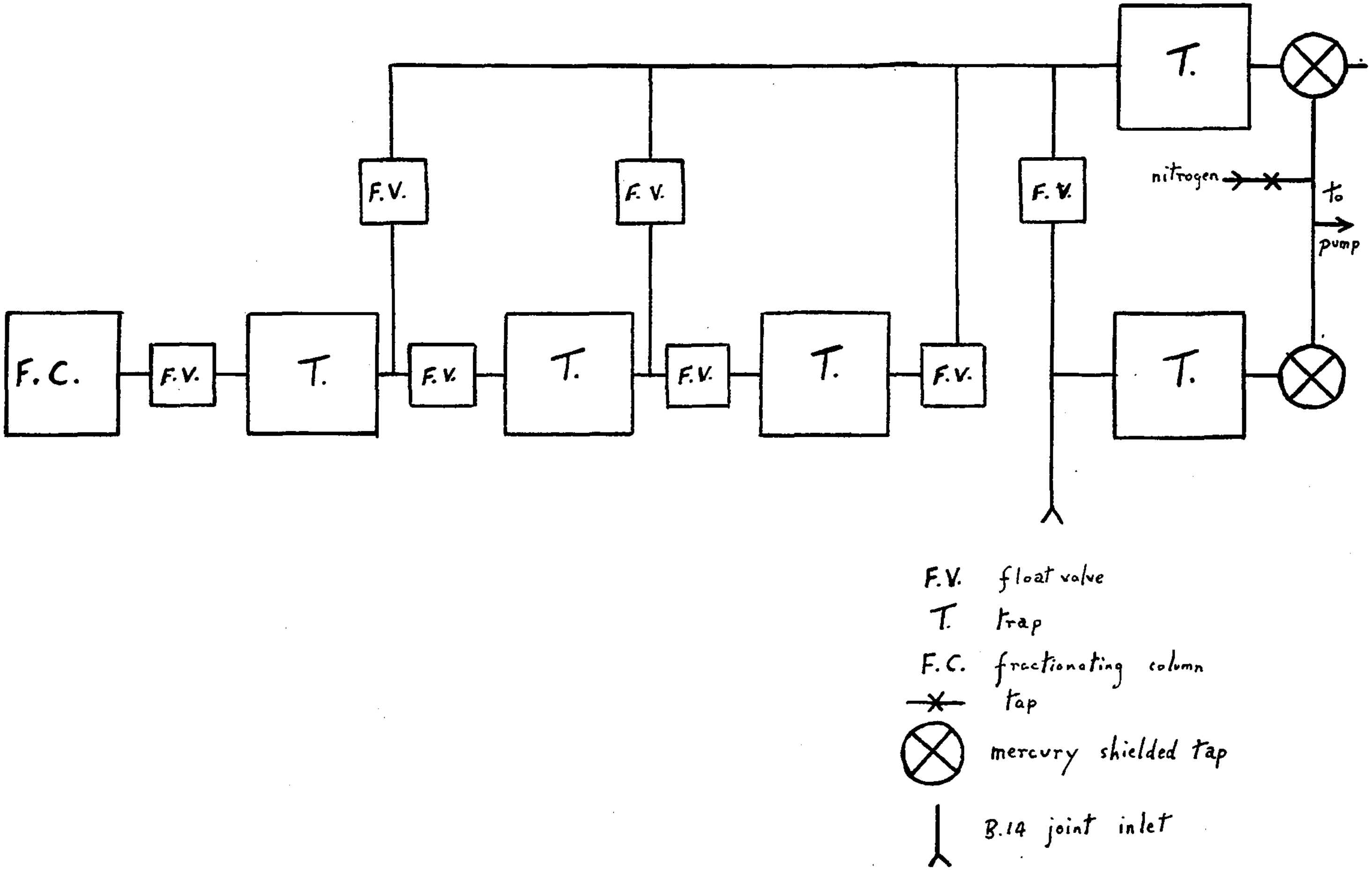
Reaction with Cacodyl Chloride

$$(CH_3)_3SnLi + (CH_3)_2AsCl = (CH_3)_3Sn\text{-}As(CH_3)_2 + LiCl.$$

The reaction between trimethyltin bromide (12.2 gms., 0.05 mole) in tetrahydrofuran (40 c.c.'s) and lithium (about 1.1 gms., about 0.15 mole) in tetrahydrofuran (60 c.c.'s) was carried out in the usual way, the solution filtered, and the amount of trimethyltin lithium found by titration (88% yield). When this solution was run into an equivalent amount of cacodyl chloride (6.2 gms., 0.044 mole) in tetrahydrofuran (~40 c.c.'s), under nitrogen, some heat was generated, the green colour disappeared, and a cloudiness developed in the solution. After removing the bulk of solvent by distillation the remaining liquid was condensed into a trap cooled in liquid nitrogen at ~ .03 mm. pressure. This was carried out to remove volatile matter from lithium halides. On working up, this liquid, however, was found to consist almost entirely of tetrahydrofuran and it was decided to repeat the reaction using double concentrations of material.

Trimethyltin lithium was prepared from trimethyltin bromide (24.4 gms., 0.1 mole) in tetrahydrofuran (40 c.c.'s) and lithium (2.3 gms., 0.3 mole) in tetrahydrofuran (~ 50 c.c.'s). The yield indicated by titration was 91%. In

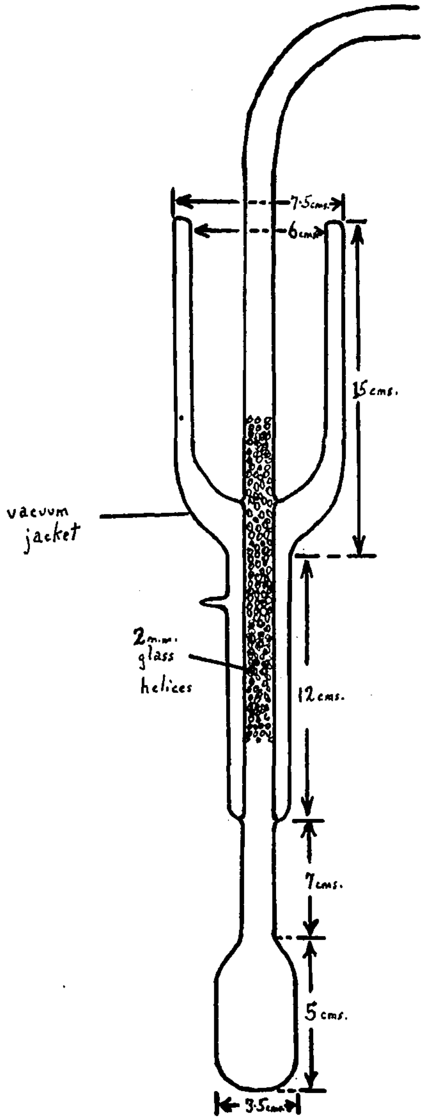
DIAGRAM OF FRACTIONATING TRAIN



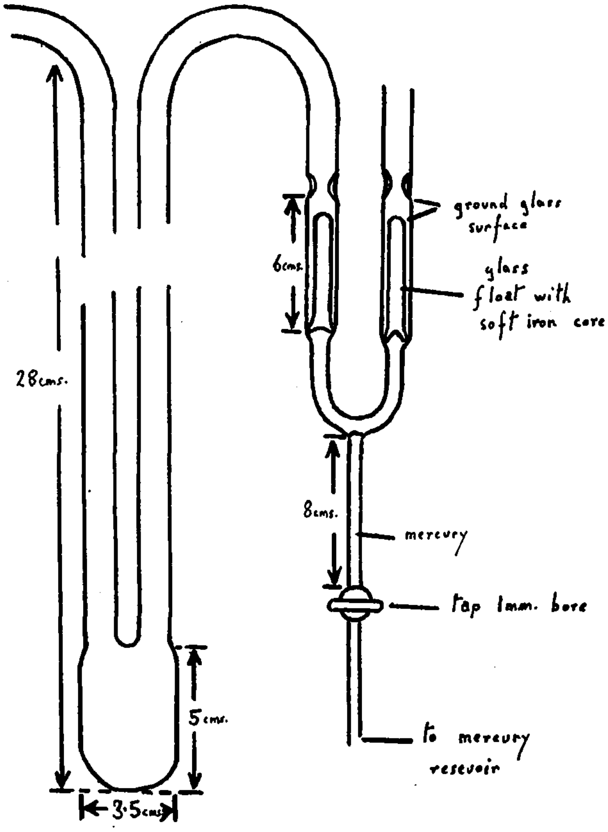
this case the lithium suspension was cooled in ice during addition of the trimethyltin bromide solution as heat was evolved. Reaction with cacodyl chloride (12.8 gms., 0.91 mole) in tetrahydrofuran (45 c.c.'s) was carried out as before, and the concentrated reaction material was condensed into a trap cooled in liquid nitrogen, at about .03 m.m. pressure, this time however the flask was heated to about 100°C. A colourless residue remained behind. From this stage onwards the material condensed into the trap was handled in a vacuum apparatus as the products of reaction were very oxygen sensitive.

Residual solvent was removed from the liquid using a small vacuum-jacketed column in the apparatus and then an attempt was made to obtain a pure component from the remaining liquid. The liquid was allowed to evaporate up the short vacuum-jacketed column, which was cooled at the top by acetone to which pieces of solid carbon dioxide were added such that the liquid refluxed steadily. Volatile products were trapped in two traps connected in series to the top of the column. The trap nearest the column was cooled to 0°C. and the other to liquid nitrogen temperature. No liquid condensed in the first trap but a mixture was obtained in the trap cooled in liquid nitrogen. When this trap was allowed to warm to room temperature it was found that besides liquid in the bottom of the trap a ring of white

VACUUM APPARATUS



FRACTIONATING COLUMN



TRAP AND FLOATVALVE

crystalline solid remained in the inlet to the trap. This slowly dissolved due to the solvent action of the liquid in the bottom of the trap. A further attempt was made to separate this mixture by allowing it to pass through a trap at $-10^{\circ}C$. and into a trap cooled in liquid nitrogen. When all the liquid had evaporated from the first trap liquid was found in both the other traps, and also a ring of white solid in the inlet to the final trap (A).

The solid in the trap was probably hexamethylditin, m.pt. $23^{\circ}C$., since cacodyl $[(CH_3)_2As-As(CH_3)_2]$ melts at $-4^{\circ}C$. The mixed compound $(CH_3)_3Sn-As(CH_3)_2$, an unsymmetrical molecule, would be expected to melt at an even lower temperature. Separation by distillation under reduced pressure would be difficult if the mixture consisted of hexamethylditin and cacodyl or even $(CH_3)_3Sn-As(CH_3)_2$, as the former two have boiling points which only differ by 12° at atmospheric pressure. It would be inadvisable to distil at atmospheric pressure as the compounds tend to decompose.

An attempt was made to estimate the relative amounts of tin and arsenic in a sample of the liquid from trap A, mentioned previously. A thin tube was attached to the vacuum system, evacuated, and some of the liquid was condensed into it by cooling in liquid nitrogen. The neck of the tube was then sealed up by heating with a hand gas-torch. After allowing the tube to warm to room temperature the tube and contents were weighed. The tube was then broken under anhydrous methyl alcohol, under nitrogen, to dissolve out the liquid. The solution was then titrated with approximately normal iodine in methyl alcohol to a permanent brown colour. By this method organo-tin and -arsenic compounds would be converted to the corresponding iodides (probably $(CH_3)_2AsI_3$, $(CH_3)_3SnI$ or $(CH_3)_2SnI_2$) which could be handled in the air. Approximately two normal sodium hydroxide (aqueous; equal to four times the volume of iodine solution used) was then added to convert the iodides to the corresponding hydroxy-compounds. The main bulk of solution was then decanted into a conical flask and the rest filtered through a weighed sintered crucible to collect the glass from the tube used to weigh out the sample. The sintered crucible was then dried to constant weight and the weight of glass obtained. Subtraction of this weight from the weight of the tube and contents gave the weight of sample (0.6270 gm.). All washings were collected in the conical flask which was then heated on a water-bath until only a small amount of liquid remained. Fuming nitric acid (25 c.c.' was added to the cooled solution which was then boiled gently. This procedure was repeated twice to ensure complete oxidation of tin to stannic oxide. The arsenic, which was expected to be present as cacodylic acid, was not expected to be oxidised as the acid was reported to be resistant to oxidation by nitric acid. The solution was diluted with distilled water (30 c.c.'s), boiled with macerated filter-paper, and left to stand for a few hours. Solid was then collected on an ashless filter-paper, washed with dilute nitric acid, the filter-paper then being transferred to a weighed silica crucible and ignited to constant weight. The solid was weighed as SnO_2 (0.1384 gm.). The solution left which was expected to contain the arsenic was made alkaline to sodium bicarbonate, then slightly acid to nitric acid and finally alkaline to sodium hydroxide (about twice normal). At this stage arsenic was expected to be present as sodium cacodylate (or if any cacodylic acid had broken down as sodium arsenate). Ammonium persulphate (32 gms.) was added and the solution was boiled for 10-15 minutes to oxidise all arsenic to arsenate. Excess persulphate was destroyed by adding two normal oxalic acid (200 c.c.'s) and boiling until a colourless solution was obtained. After cooling, the solution was saturated with sulphur dioxide to reduce any arsenic to the trivalent state. Excess sulphur dioxide was boiled off, and the solution chilled by ice-water was saturated with hydrogen sulphide gas. No precipitate of arsenic trisulphide was obtained. By this method the amount of tin found in the sample was 16.7%. The calculated amount of tin in $(CH_3)_3Sn-As(CH_3)_2$ is 42.6%. The arsenic presumably was lost during estimation.

(e) Reactions with Sodium Methylsulphide and Sodium Methylselenide

Reaction between Sodium Methylsulphide and Trimethyltin Bromide

Methyl mercaptan was prepared by the method of Windus and Shildneck.[12] A 250 c.c. three-necked flask was fitted with a dropping funnel, a reflux condenser, and a nitrogen inlet leading to the bottom of the flask. The end of the condenser was connected in series to:- a safety trap, consisting of an empty 100 c.c. flask, another 100 c.c. flask containing sulphuric acid (concentrated), a tower containing calcium chloride and an empty flask (100 c.c.) which acted as a trap; a 250 c.c. flask containing sodium (2 gms., .0875 mole) in methyl alcohol (40 c.c.'s); an empty flask (100 c.c.) and a flask (100 c.c.) containing saturated lead acetate (20 c.c.'s).

Methyl <u>iso</u>thiourea sulphate (13.9 gms, .05 mole) was placed in the three-necked flask, a slow current of nitrogen was blown through the apparatus, while sodium hydroxide (4 gms, 0.1 mole) in water (40 c.c.'s) was added to the methyl <u>iso</u>thiourea sulphate from the dropping funnel. The solution was warmed gently for 1½ hours to generate methyl mercaptan. The reaction was completed by heating more vigorously for twenty minutes. The solution of sodium in methyl alcohol, which was weighed before reaction, was then re-weighed. The increase in weight was due to the methyl mercaptan absorbed

(3.5 gms., .073 mole).

$$(CH_3)_3SnBr + CH_3SNa = (CH_3)_3SnSCH_3 + NaBr.$$

The flask containing the absorbed methyl mercaptan was fitted with a stirrer, dropping funnel and a reflux condenser. Trimethyltin bromide (18.5 gms., .076 mole) in methyl alcohol (40 c.c.'s) was added slowly with stirring. The solution was concentrated by distilling off solvent and then volatile material at ~ .03 m.m. pressure was condensed in a trap cooled in liquid nitrogen, the reaction vessel being heated to about 70°C. This separated organic matter from sodium bromide. The liquid collected in the trap was redistilled to remove more solvent and then an attempt was made to distil the residual liquid at 5 m.m.'s, when sublimation was observed to occur. An attempt to collect this sublimate at 5 m.m.'s proved unsuccessful as the solid was moistened by the liquid present. The liquid was, however, successfully distilled at 3.5 m.m.'s most boiling at 33.5-34.5°C. and no liquid boiling above 43.5°C. was collected. Solid remained behind in the flask. As the amount of liquid distilled was small and was suspected to be the desired compound the reaction was repeated. The solid which sublimed was probably trimethyltin hydroxide, which sublimes at 80°C. and melts at 118°C. Slight fuming was noticed to occur when the liquid was exposed to the air.

Methyl mercaptan was prepared, as before, by the reaction between methyl isothiourea sulphate (27.8 gms., 0.1 mole) and sodium hydroxide (8 gms., 0.2 mole) in water (80 c.c.'s). This time, however, the dried methyl mercaptan was collected in a trap cooled by a solid carbon dioxide acetone mixture. The mercaptan was then transferred and stored in the vacuum system. Methyl mercaptan was then condensed into a trap, into which a solution of methyl alcohol (40 c.c.'s) containing sodium (2.4 gms., .107 mole) was run. The volume of methyl mercaptan was calculated approximately from the volume of the storage vessel and pressure of gas such that an excess of mercaptan was present. This was to ensure that complete formation of sodium methylsulphide occurred, e.g.,

$$CH_3ONa + CH_3SH = CH_3OH + CH_3SNa,$$

as otherwise the compound $(CH_3)_3SnOCH_3$ might be formed:-

$$CH_3ONa + CH_3SnBr = (CH_3)_3SnOCH_3 + NaBr.$$

Trimethyltin bromide (26 gms. .107 mole) in methyl alcohol (60 c.c.'s) was then run slowly into the stirred solution of sodium methylsulphide. This reaction was carried out under nitrogen to prevent any reaction with air or moisture. The reaction mixture was worked up as before and distilled finally at 3.5 m.m.'s. Some solid again tended to sublime and solid remained behind in the distilling flask, melting point 110°-112°C. (trimethyltin hydroxide m.pt. 118°C.). The liquid collected was redistilled at 3.5 m.m.'s using a small vacuum-jacketed column, three main fractions were collected:-

1) 31.5 - 32.5°C., 1.2 gms.)
2) 32.5 - 33°C., 3.4 gms.) total 6.1 gms.
3) 33°C., 1.5 gms.)

Samples of the middle fraction were used for analysis.

Analysis:-

Tin

Tin was estimated using the method of Gilman and King described on page 95.

Sulphur

The sulphur was estimated by making use of the fact that methyl mercaptan was liberated from the compound by the action of dilute acid.

A weighed sample of liquid was mixed with bench diluted hydrochloric acid (10 c.c.'s) and the methyl mercaptan liberated was carried by a stream of nitrogen bubbled through the solution into four traps containing mercuric cyanide (4% by weight). The precipitate of $(CH_3S)_2Hg$ was filtered off and weighed after drying over phosphorus pentoxide *in vacuo*.

Carbon and hydrogen were estimated in the usual way.

Element	Observed	Calculated for $(CH_3)_3SnSCH_3$
% Sn	55.94	56.35
% S	15.85	15.19
% H	6.16	5.70
% C	23.49	22.78

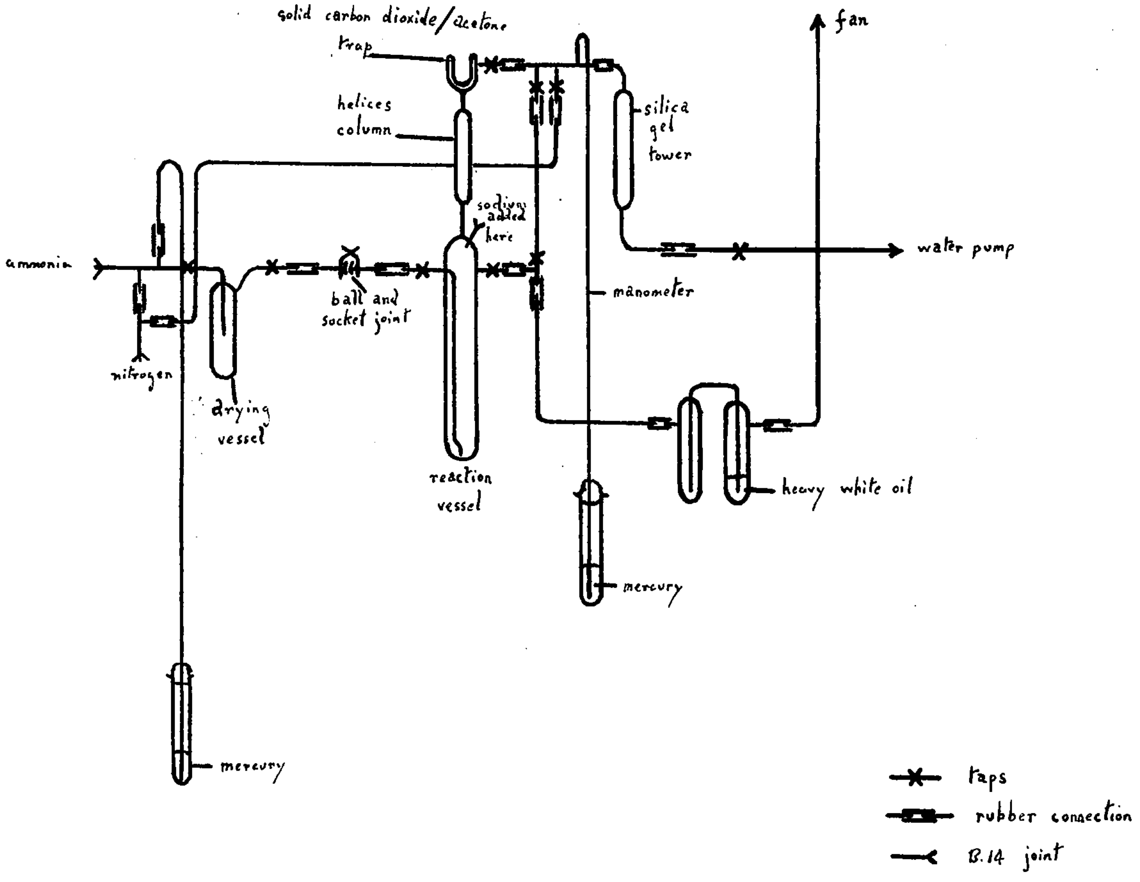
The preparation of $(CH_3)_3SnSCH_3$ was confirmed. The yield of product based on the three main fractions collected at 3.5 m.m.'s was 27%.

Reaction between Sodium Methylselenide and Trimethyltin Bromide

$$CH_3SeNa + (CH_3)_3SnBr = (CH_3)_3SnSeCH_3 + NaBr$$

Dimethyl diselenide ($CH_3SeSeCH_3$) was prepared as described by Bird and Challenger.[13] Selenium (64 gms., 0.81 mole) was completely dissolved in a mixture of sodium hydroxide (32 gms. 0.8 mole) and sodium formaldehyde-sulphoxylate (50 gms., 0.42 mole) in water (500 c.c.'s) in a three-necked one litre flask fitted with a stirrer, condenser and a dropping funnel. Methyl sulphate (44 c.c.'s, 0.34 mole) was added and after heating for one hour the reddish-brown colour had almost completely gone and a heavy oil separated. This was extracted with chloroform, dried over anhydrous sodium sulphate and fractionated to give the diselenide as an orange oil. 22 gms. of diselenide b.pt. 56-59°C./21 m.m.'s was collected (30% yield).

DIAGRAM OF LIQUID AMMONIA SYSTEM

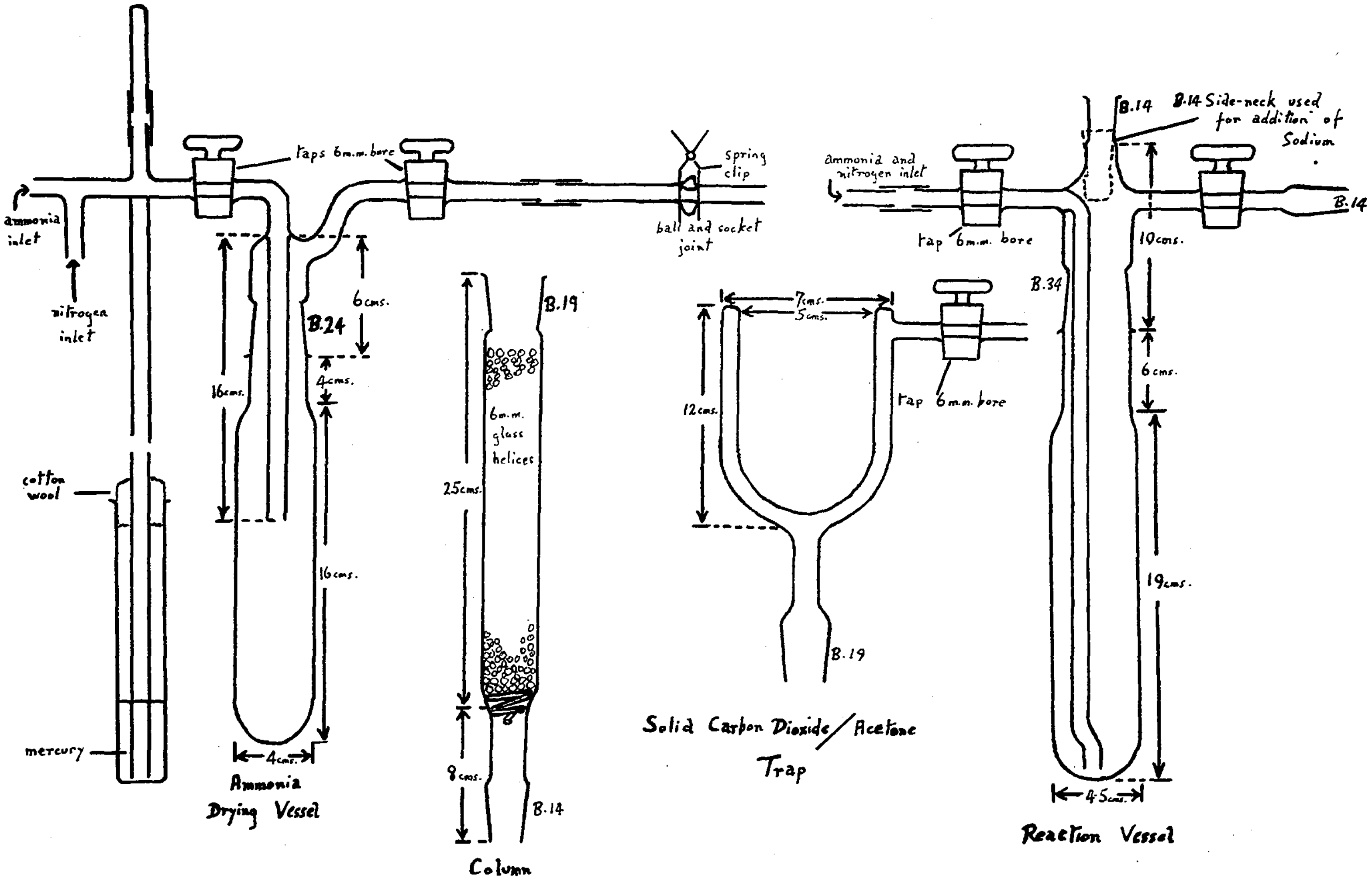


Sodium methylselenide was prepared in liquid ammonia. Ammonia was dried by distilling from sodium and condensing in a reaction vessel cooled by a solid carbon dioxide/acetone trap. Sodium (2.2 gms., .096 mole) was then added. A solution of methyl diselenide (9.4 gms., .05 mole) in tetrahydrofuran (10 c.c.'s) was run slowly into the liquid ammonia solution, keeping the latter well agitated by bubbling nitrogen through it. When the bulk of diselenide had been added the remaining solution was diluted by the addition of more tetrahydrofuran (~ 10 c.c.'s). This solution was added dropwise until the blue colour due to the sodium disappeared, leaving a slightly cloudy rose-pink solution:-

$$CH_3SeSeCH_3 + 2Na = 2CH_3SeNa.$$

More tetrahydrofuran (50 c.c.'s) was added and the bulk of the ammonia was allowed to boil off, by removing the cooling bath from the reaction vessel. A short helices column was then fitted to the top of the reaction vessel (in place of the dropping funnel). At the top of this column a solid carbon dioxide/acetone trap was fitted to condense tetrahydrofuran while allowing ammonia to be removed <u>via</u> the water pump. In this way a mixture of sodium methylselenide in tetrahydrofuran was obtained, the apparatus being refilled by nitrogen. The ammonia was removed to prevent any ammonolysis of products. A cloudy yellow solution with

APPARATUS USED FOR REACTIONS IN LIQUID AMMONIA



yellow solid at the bottom remained behind in the reaction vessel. A solution of trimethyltin bromide (23 gms., .094 mole in tetrahydrofuran (40 c.c.'s) was added such that the mercaptide was in slight excess. Some heat was generated and the yellow colour and solid disappeared being replaced by a white solid.

The mixture was transferred, under nitrogen, to a flask from the reaction vessel, concentrated, and volatile matter condensed into a trap cooled in liquid nitrogen, *in vacuo*, in order to separate from the inorganic salts. The flask was heated to ~ 100°C. This liquid was then distilled, under nitrogen, to remove more tetrahydrofuran and the remainder was distilled at 5.5 m.m.'s, most of the liquid boiling at ~ 48°C. The liquid was pale yellow in colour. This liquid was then redistilled using a small vacuum-jacketed column at 5.3 m.m.'s, the following separate fractions being collected:-

1) up to 46.5°C.
2) 46.5 - 47°C., 3 gms.,
3) 47 - 47^{+}°C., 3.7 gms.
4) 47^{+} - 47.4°C., 4.2 gms.
5) 47.4 - 47.8°C.)
) 6.0 gms.
6) 47.8 - 48°C.)

The last five fractions boiled within 1.5° this presumably being due to small changes in pressure. The total weight of the five fractions was 16.9 gms. Samples of 3) were used for analysis.

Analysis

Tin analyses were carried out by the method of Gilman and King as described on page 95 . One of the results was ~0.6%* low this being due to slight spattering of solid while boiling off concentrated sulphuric acid.

Carbon and hydrogen were analysed in the usual way.

Element	Observed	Calculated for $(CH_3)_3SnSeCH_3$
% Sn	45.41*; 46.30	46.07
% C	18.98	18.62
% H	5.11	4.66

The formation of $(CH_3)_3SnSeCH_3$ was confirmed. The yield (based on the trimethyltin bromide used) was 69.5%

(f) Reactions of Cacodyl and Sodium in Liquid Ammonia

Preparation of Cacodyl

Cacodylic acid [$(CH_3)_2AsOOH$, 55.2 gms., 0.4 mole] in water (100 c.c.'s) was placed in a 250 c.c. three-necked flask fitted with a stirrer (with a nitrogen inlet), dropping funnel and condenser. Sodium hypophosphite ($NaH_2PO_2.H_2O$, 37 gms., 0.31 mole) in concentrated hydrochloric acid (33 c.c.'s) was added, as a suspension in one portion as little heat was generated initially. After a few minutes the solution became cloudy and heat was evolved. The flask was then cooled in water. After stirring for two hours the mixture was blown out of the flask into a dropping funnel, under nitrogen, where the bottom layer was run into a flask, under nitrogen, containing calcium sulphate. The dried liquid was redistilled at 17 m.m.'s, a small amount of liquid (4.5 gms.) boiled at 49°C., the rest was condensed in a liquid nitrogen trap connected to the system (Literature:-[14] Cacodyl b.pt. 43.8-44.4°C./11 m.m.'s). The liquid which distilled at 49°C. was inflammable in air (cacodyl) but the liquid collected in the trap was not (probably cacodyl chloride).

As the yield of cacodyl was small (11%) another preparation was attempted using a modified procedure. Sodium hypophosite ($NaH_2PO_2.H_2O$, 54 gms., 0.5 mole) was dissolved in water (50 c.c.'s) and concentrated hydrochloric acid (50 c.c.'s) was added slowly. The mixture was filtered (to remove sodium chloride) and poured into the reaction vessel used previously. To the stirred solution, under nitrogen, was added a solution of cacodylic acid (27.6 gms., 0.2 mole) in water (36 c.c.'s). Cloudiness developed after a few minutes and the solution was kept warm by slow addition of the cacodylic acid solution ($\sim 2\frac{1}{4}$ hours). After cooling, the mixture was blown into a dropping funnel, as before, separated, and the heavy liquid dried and distilled. 16.1

gms. of liquid b.pt. 54.5°C./19.5-20 m.m.'s was collected (77% yield).

The aqueous hypophosphorous acid solution from the reaction was replaced in the reaction vessel and all the distilled liquid collected in the first reaction was run into it. The heavy layer produced was then worked up as in the second reaction. 11.5 gms. of liquid b.pt. 53°C./18-18.5 m.m.' was obtained (28% yield).

There was no indication of formation of cacodyl chloride in this case or the previous reaction.

Reaction of Dimethylarsenic Sodium with n-Propyl Halides

$$(CH_3)_2AsAs(CH_3)_2 + 2Na = 2(CH_3)_2AsNa$$

$$(CH_3)_2AsNa + \underline{n}\text{-}C_3H_7I = (CH_3)_2\underline{n}\text{-}C_3H_7As + NaI$$

$$(CH_3)_2\underline{n}\text{-}C_3H_7As + CH_3I = (CH_3)_3\underline{n}\text{-}C_3H_7AsI$$

The object of these reactions was to investigate the formation of dimethylarsenic sodium in liquid ammonia with a view to the use of this reagent to form tin-arsenic bonds. Ammonia was dried by distilling from sodium and condensed into the reaction vessel. Sodium (0.7 gms., .034 mole) was added to the liquid ammonia. A solution of cacodyl in ether (20 c.c.'s) was run into the ammonia until the blue colour of the sodium was displaced. The end point was uncertain as the colour change from blue to a dark-brown was not sharp but changed gradually as the cacodyl was added. Ammonia was removed as in the preparation of sodium methylselenide in liquid ammonia (page 38). n-Propyl iodide (5.2 gms., .034 mole) in ether (40 c.c.'s) was then added to the reaction vessel. The reaction vessel had to be cooled at this stage as considerable heat was evolved. Volatile products were then condensed, in vacuo, into a trap cooled in liquid nitrogen, to separate from inorganic salts. Then the contents of the trap were transferred to a flask, under nitrogen, and a solution of methyl iodide (4.3 gms., .034 mole) in ether (40 c.c.'s) was added. After this stage working up was carried out in air as the products were no longer oxygen sensitive. Solid (2 gms.) was filtered off from the concentrated ether solution. After repeated recrystallisation from alcohol the melting point was 207°C. ($(CH_3)_3$n-C_3H_7AsI, m.pt. 211°C.). The solid (2 gms.) represented a 23% yield of $(CH_3)_3$n-C_3H_7AsI.

As the yield was small the reaction was repeated using n-propyl bromide instead of n-propyl iodide. The arsonium iodide obtained in this case was much purer, m.pt. 210-211°C., after crystallising twice from absolute alcohol. The arsonium iodide obtained (2.9 gms.) represented a yield of 26%.

Reaction between Dimethylarsenic Sodium and Trimethyltin Bromide

As in the previous reactions a solution of cacodyl in ether (10 c.c.'s) was run into a solution of sodium (1 gm.,

.044 mole) in liquid ammonia. Although the blue colour of the sodium changed to green and then brown the end point was sharp. The solution suddenly turned a bright, clear, orange-red colour. Addition of trimethyltin bromide (10.65 gms., .044 mole) in ether (10 c.c.'s) caused immediate precipitation of white solid, the solution becoming pale yellow in colour. The ammonia was not removed in this reaction as organo-tin halides are not ammonolysed by ammonia and the products of reaction which might occur, _e.g._, $(CH_3)_3SnSn(CH_3)_3$, $(CH_3)_2AsAs(CH_3)_2$ and $(CH_3)_3SnAs(CH_3)_2$, would also be stable to liquid ammonia. Ammonia was allowed to boil off and then the reaction mixture was transferred to a flask, under nitrogen, where the mixture was concentrated by removal of ether. Volatile materials were then condensed into a trap cooled in liquid nitrogen, _in vacuo_, to separate from inorganic halides. More ether was distilled from this liquid, under nitrogen, and then the residue was distilled at 16-17 m.m.'s. A fraction, boiling point 58-66°C. was collected. A second fraction boiling 59.5-61°C./10 m.m.'s was also collected. In this case an air condenser was used as solid formed in the water condenser. Little liquid remained undistilled. On standing, under nitrogen, solid was observed to form in both fractions.

The second fraction was redistilled at 9.4 m.m.'s but no steady boiling point was observed indicating the presence of a mixture. A sample of some of this liquid was used to try to ascertain the relative amounts of tin and arsenic. The results were not quantitative but indicated the presence of more tin than arsenic.

As in the previous reaction between tin and arsenic no single product was obtained. In the preparation of cacodyl the following boiling points had been observed, 54.5°C./19.5-20 m.m.'s and 53°C./18-18.5 m.m.'s, however, the first fraction in the reaction mixture distilled at 58°C/16-17 m.m.'s, which was probably caused by distillation of cacodyl with a slightly less volatile material. The presence of another component was suggested by the formation of a low melting substance. This in turn suggested formation of hexamethylditin, m.pt. 23°C. Thus it seemed probable that a mixture of cacodyl, hexamethylditin and probably $(CH_3)_3Sn-As(CH_3)_2$ had been formed. As in the previous reaction between tin and arsenic it was impossible to separate any one component because of the similarity of boiling points. In view of this fact, and the fact that a mixture had resulted from the reaction this line of approach was abandoned.

(g) Reactions with Tri-n-Butyltin Lithium

Preparation of Anhydrous Stannous Chloride[15]

A mixture of acetyl chloride (160 c.c.'s) and acetic anhydride (250 c.c.'s) was added slowly to stannous chloride dihydrate (86 gms., 0.38 mole). The mixture was then refluxed for two hours. The liquid at this stage was a light brown in colour. After cooling the mixture was filtered and the solid washed twice with dry ether to remove any residual acid chloride or anhydride. The solid was then placed in a vacuum desiccator for two hours over phosphorus pentoxide. Finally the solid was heated by toluene vapour in a drying pistol, <u>in vacuo</u>, for two hours. A sintered plate was placed in the apparatus to prevent solid being drawn into the pump. The anhydrous stannous chloride was then sealed in tubes in approximately twenty gram quantities and used as required.

Reaction with Trimethylchlorsilane

Lithium (7.5 gms., 1.07 mole) was converted to shot in the way described on page 13, and added with ether (100 c.c.'s) to a 500 c.c. three-necked flask fitted with a stirrer (containing a nitrogen inlet), dropping funnel and a thermometer. n-Butyl lithium was prepared by the following method.[16] A solution of n-butyl bromide (51.4 gms., 0.375 mole) in ether (100 c.c.'s) was added to the stirred suspension of lithium keeping the mixture at -10°C. by means of a solid carbon dioxide/acetone bath at about -40°C. When all the n-butyl bromide solution had been added the reaction mixture was allowed to warm to 0°C. for 1½ hours. The solution was then poured through a polythene tube, containing a glass-wool plug, into a graduated dropping funnel. The yield of n-butyl lithium was then calculated by titration of a 2 c.c. aliquot, after hydrolysis, with normal hydrochloric acid. A blank was carried out by adding a sample to dry ether containing benzyl chloride.[17] After standing for a few seconds the solution was hydrolysed and titrated with normal hydrochloric acid. The difference of the two titers represented a measure of the amount of n-butyl lithium. The blank measured alkali other than n-butyl lithium, which was removed as shown:-

$$\underline{n}\text{-}C_4H_9Li + C_6H_5CH_2Cl = C_6H_5\,CH_2Li + \underline{n}\text{-}C_4H_9Cl$$

$$C_6H_5CH_2Li + C_6H_5CH_2Cl = C_6H_5CH_2CH_2C_6H_5 + LiCl.$$

The yield of n-butyl lithium was 85%.

Based on this, a weight of stannous chloride (18.6 gms., .098 mole), which was equivalent to 200 c.c.'s of the above solution, was stirred in a flask with ether (100 c.c.'s) under nitrogen. The n-butyl lithium was run into the suspension at about -50°C.

$$3\underline{n}\text{-}C_4H_9Li + SnCl_2 = (\underline{n}\text{-}C_4H_9)_3SnLi + 2LiCl.$$

An equivalent amount of trimethylchlorsilane (10.7 c.c.'s, .098 mole) in ether (100 c.c.'s) was then added to the mixture in accordance with the equation:-

$$(\underline{n}\text{-}C_4H_9)_3SnLi + (CH_3)_3SiCl = (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Si(CH_3)_3 + LiCl.$$

The initial deep-brown colour of the solution remained unchanged after standing overnight. A small sample exposed to air became paler in colour.

The solution was stirred with water to remove lithium halides. The two layers were separated, the ether layer being dried over anhydrous magnesium sulphate, and ether distilled off under nitrogen. A pale orange solution remained. This solution was then pumped to 1 m.m. for about 45 minutes and all volatile matter collected in a trap cooled in liquid nitrogen. The liquid collected was colourless. On distillation, under nitrogen, through a short vacuum-jacketed column most liquid boiled between 87° and 90°, especially at the latter temperature (trimethylsilanol, b.pt. 90.5°C). The amount of liquid obtained, assuming it to be trimethylsilanol, represented over 70% of the silicon used in the reaction.

An attempt to distil the orange liquid at 0.1 m.m. was unsuccessful, as bumping occurred, and very little liquid distilled.

Tests for tin were carried out on the volatile material and the orange solution. Tin was present in the orange liquid but not in the volatile liquid.

In view of the fact that little reaction appeared to have taken place with trimethylchlorsilane (recovery of trimethylsilanol) another reaction was carried out using more rigorous conditions.

Tri-n-butyltin lithium was prepared as previously using similar quantities of materials (yield of n-butyl lithium 83.9%). The amount of stannous chloride used was 17.4 gms. (0.092 mole). The equivalence point of addition of n-butyl lithium to the stannous chloride was determined by application of the colour test[18] with p-bromodimethylaniline. This only becomes positive when a slight excess of n-butyl lithium is present. The calculated quantity of trimethylchlorsilane (11.5 c.c.'s, 0.92 mole) in ether (100 c.c.'s) was then added to the solution at about -40°C. No colour change was observed.

Ether was removed by distillation at atmospheric pressure, under nitrogen. The residual mixture was then evacuated to 0.1 m.m. and volatile material collected in a trap cooled in liquid nitrogen. This liquid (A) was then distilled, under nitrogen, and a main fraction boiling point 114°C. (6.4 gms.) was collected; about half the liquid did not distil. This liquid was then left while the orange coloured liquid was examined as trimethylsilyltri-n-butyltin ($(CH_3)_3Si\text{-}Sn(n\text{-}C_4H_9)_3$) was expected to be present.

The coloured solution was pumped to about .02 m.m. and heated to about 145°C. but only 2 gms. of liquid was collected in a trap cooled in liquid nitrogen. As none of the expected product had been obtained in appreciable yield the residual coloured mixture was washed into a beaker of water with alcohol. The resultant mixture was extracted with benzene. After drying over magnesium sulphate, benzene was removed by distillation. The residual liquid (B) was distilled at 3.5 m.m.'s, a fraction boiling point 130°-150°C. being collected. On redistillation of this liquid at 2.9 m.m.'s the following fractions were collected:-

1) up to 122.5°C., 1.2 gms.
2) 122.5-123.5°C, 1.9 gms.
3) 123.5°C., 1.2 gms.

Fractions 1) and 3) were slightly cloudy. Samples of 2) were used for estimation of tin and silicon. Weighed samples were broken down and ignited to constant weight by the method of Gilman and King as described on page 95. The residue was weighed as SnO_2 and SiO_2. The tin was removed by repeated heating with ammonium iodide leaving behind silica. The values obtained, however, were not consistant with the formula $(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Si(CH_3)_3$, the tin value being of the right order but the silicon being almost negligible. This, together with the fact that the percentage of tin was similar to that in $(\underline{n}\text{-}C_4H_9)_4Sn$ as well as $(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Si(CH_3)_3$ ($(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Si(CH_3)_3$, 32.73% tin), suggested that the liquid was probably tetra-n-butyltin, although this was reported[1] to boil at 130°C/2 m.m.'s. Further confirmation was obtained from carbon and hydrogen analysis.

	%C	%H
$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Si(CH_3)_3$	49.64	9.93
$(\underline{n}\text{-}C_4H_9)_4Sn$	55.38	10.39
Sample	54.80	11.60

The identity of the liquid (B) was confirmed by the following method. A weighed sample of liquid was dissolved in methylene chloride and standard bromine in methylene chloride was added in accordance with the equation:-

$$(\underline{n}\text{-}C_4H_9)_3SnSi(CH_3)_3 + Br_2 = (CH_3)SiBr + (\underline{n}\text{-}C_4H_9)_3SnBr,$$

assuming the sample to be $(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Si(CH_3)_3$. The solution was coloured when all the bromine had been added but the colour disappeared on standing (about 48 hours). Volatile material at 2 m.m.'s was then condensed into a trap cooled in liquid nitrogen, keeping the liquid mixture at room temperature. At this pressure trimethylbromsilane b.pt. 80°C. (and methylene chloride) would condense into the trap leaving behind tetra-n-butyltin. The solution from the trap was washed out with water and methyl red was added. Two drops of 0.1N potassium hydroxide were found to colour the solution yellow indicating an excess of alkali. This in turn indicated absence of acid (hydrogen bromide), and consequently absence of trimethylbromsilane,

$$(CH_3)_3SiBr + H_2O = (CH_3)_3SiOH + HBr.$$

This suggested the absence of $(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Si(CH_3)_3$. The methylene chloride was treated with thiourea and picric acid in order to obtain an <u>iso</u>thiouronium picrate from any <u>n</u>-butylbromide (b.pt. 101.4°C.) present. This would be obtained from tetra-<u>n</u>-butyltin on treatment with bromine. The product obtained was purified and a mixed melting point with authentic <u>n</u>-butyl<u>iso</u>thiouronium picrate obtained. The sample melted at 175°C; the authentic specimen melted at 174-5°C. and the mixed melting point was 175°C. An acetate was prepared from the liquid left behind in the reaction vessel by shaking an ethereal solution of it with potassium hydroxide solution and heating the residue left after removal of ether with glacial acetic acid at 125°C. The product was purified by recrystallisation from 40°-60° petroleum ether. An authentic specimen of tri-<u>n</u>-butyltin acetate was also prepared.[19] The acetate obtained from the reaction melted at 83-84°C; the authentic specimen of tri-<u>n</u>-butyltin acetate melted at 83.5-84°C. and the mixed melting point was 83-84°C. This confirmed the absence of $(\underline{n}\text{-}C_4H_9)_3SnSi(CH_3)_3$ and presence of tetra-<u>n</u>-butyltin. It was found also that if the oxide obtained from a weighed sample of the liquid (B) was assumed to be stannic oxide and not a mixture of stannic oxide and silica the percentages of tin were 34.29% and 34.79%. The percentage of tin in tetra-n-butyltin is 34.25%.

The amount of tin recovered as tetra-n-butyltin from the reaction (weight of fractions boiling at 2.9 m.m.'s, 4.3 gms.) was 15%.

The low boiling liquid (A) ~ 114°C. was then examined. It was first distilled through a short helices column and the greater part of it boiled at 116-116.5°C. The properties of this liquid were not consistent with those of hexamethyldisilane, a possible product, as this liquid did not freeze at 12°C. and its refractive index was of the wrong magnitude. However, in view of the fact that reaction had involved use of n-butyl lithium the formation of n-butyltrimethylsilane was then considered, e.g.,

$$(CH_3)_3SiCl + n\text{-}C_4H_9Li = n\text{-}C_4H_9(CH_3)_3Si + LiCl.$$

The liquid had very similar properties to n-butyltrimethylsilane.

	Boiling Point	Refractive Index
$(CH_3)_6Si_2$	112°-114°C.	$1.4207_D^{24.4}$
$n\text{-}C_4H_9(CH_3)_3Si$	115.3°-115.5°C.	1.4030_D^{20}
Sample	116°-116.5°C.	$1.4032_D^{19.5}$

Values obtained for carbon and hydrogen confirmed the formation of n-butyltrimethylsilane.

	%C	%H
$(CH_3)_6Si_2$	49.25	12.40
n-$C_4H_9(CH_3)_3Si$	64.60	13.92
Sample	65.19	13.75

The amount of n-butyltrimethylsilane obtained (6.4 gms.) represented 54% of the silicon used in the reaction.

Reaction with Methyl Iodide

n-Butyl lithium was prepared in the usual way using similar quantities of materials used previously (yield of n-butyl lithium 83.1%). The solution of n-butyl lithium was then added to stannous chloride (18.1 gms., .095 mole) in ether (100 c.c.'s) until the colour test with p-bromdimethylaniline became positive.[18] To the resulting solution at about -40°C. there was added methyl iodide (15 gms., .011 mole) in ether (25 c.c.'s), 10% excess in accordance with the equation:-

$$(\text{n-}C_4H_9)_3SnLi + CH_3I = (\text{n-}C_4H_9)_3CH_3Sn + LiI.$$

The solution changed from a deep-brown colour to yellow almost immediately on addition of the methyl iodide. When the solution was allowed to warm to room temperature the colour of the solution became a pale grey. On refluxing the solution became brown.

Lithium halides were removed by stirring the solution, under nitrogen, with water (200 c.c.'s). The aqueous layer was then removed. Some grey solid, insoluble in either layer, was collected in the aqueous layer. The dried ether layer was filtered and concentrated by distillation under nitrogen using a short helices column. A clear deep red liquid remained. Liquid (A) distilling up to 98°C. was then collected at 2 m.m.'s. This liquid weighed 6.9 gms. The distillation at this pressure was expected to remove tri-n-butylmethyltin. Although the temperature of the distilling flask was raised to about 180°C. no liquid b.pt. 130°C./2 m.m.'s corresponding to tetra-n-butyltin was collected. The remaining liquid was deep red in colour.

The liquid (A) was redistilled at 9.8 m.m.'s when a lower boiling fraction (B) boiling up to 124°C. was collected (tri-n-butylmethyltin, b.pt. 121°C./10 m.m.'s). On redistillation of the liquid (B) at 9.6 m.m.'s the following fractions were collected:-

1) up to 84°C.
2) 84-88°C.
3) 88-90°C, 1.1 g. 1), 2) and 5) weighed 1.2 g.
4) 90-91.5°C, 0.7 g.
5) 91.5-98°C.

These lower boiling fractions did not contain tin, but higher boiling fractions obtained from liquid (A) at 10 m.m.'s contained tin:-

1) up to 120°C.
2) 120-122°C./10 m.m.'s, 0.8 g.
3) 122-123°C./10 m.m.'s, 0.9 g.
4) 123-125°C./10^+m.m.'s, 2.7 g.
5) 125-127°C./10^+m.m.'s.

A sample of 4) was used for tin analysis. The tin was estimated volumetrically by the method described on page 97. The percentage of tin found in the sample was 38.64%. The calculated percentage of tin in tri-n-butylmethyltin is 38.91%. The yield of tri-n-butylmethyltin, based on the combined weights of fractions 2), 3), and 4) (4.4 gms.) was 14.4%.

A sample of the red liquid was found to deposit a white solid in air, which was probably due to formation of di-n-butyltin oxide from di-n-butyltin. As this red liquid was suspected to contain di-n-butyltin an attempt was made to characterise it by means of formation of di-n-butylmethyltiniodide,

$$(\underline{n}\text{-}C_4H_9)_2Sn + CH_3I = (\underline{n}\text{-}C_4H_9)_2CH_3SnI.$$

The remaining red solution was therefore refluxed gently with methyl iodide, under nitrogen, until the solution was almost colourless (about 2 days). The mixture from the reaction was shaken in ether with sodium hydroxide solution, and, after removal of ether, the residue was treated with acetic acid and heated to about 125°C. After working up a solid was obtained which melted at 80°C, although softening occurred below this temperature and the final melt was not clear. As the melting point was close to that of tri-n-butyltin acetate (83.5-84°C.) a mixed melting point with authentic tri-n-butyltin acetate was tried but the result was inconclusive, there being no indication of an increase in the melting point of the solid. The white solid obtained by oxidation in air was also treated with acetic acid. Again on working up a solid was obtained, which melted at 82°C. Further recrystallisation did not improve this melting point. A mixed melting point with authentic tri-n-butyltin acetate was again not decisive. The formation of the solid acetates from material in the red liquid, which appeared to be impure tri-n-butyltin acetate, suggested the presence of some tri-n-butyltin compound in the red liquid.

As the amount of tin recovered from the reaction was small (14.4%) an attempt was made to account for the rest of the tin. Even taking into account the red liquid, which was suspected to be mainly di-n-butyltin, only half the tin used in the reaction could be accounted for. An estimation of tin in the aqueous solution (used to remove lithium halides from the ether) by the volumetric method (page 97) showed that the amount of tin present was very small. It was noticed that the liquid collected in a trap cooled in liquid nitrogen during the first distillation at 2 m.m.'s, mainly residual ether, and the ether distilled from the reaction mixture had small amounts of solid in them. This solid had formed on exposure to air and was found to contain tin. The only possible tin compounds which could be volatile enough to come over with ether would be tin hydrides.

Reaction with Carbon Dioxide

n-Butyl-lithium prepared from n-butylbromide (51.4 gms., 0.375 mole) and lithium (7.5 gms., 1.07 mole) was added to stannous chloride (17.5 gms., 0.092 mole) in ether (100 c.c.'s) until the colour test with p-bromdimethylaniline became positive.[18] This occurred when 15 c.c.'s less than the calculated amount of n-butyl lithium solution had been added. Carbon dioxide was then bubbled into the solution, which was stirred continuously at -10° to -20°C. for 3½ hours. By this time the original deep red colour had disappeared, giving place to a lighter orange coloured solution containing solid matter. On standing, unstirred, a clear orange-red supernatant liquid formed. The mixture was stirred, under nitrogen, with water (125 c.c.'s), some heat being generated initially and solid appeared to be thrown out of solution. The whole mixture was filtered under nitrogen. An attempt to dissolve the solid in chloroform proved unsuccessful. After filtration the two layers were separated. The ether layer, kept under nitrogen, was orange-red in colour.

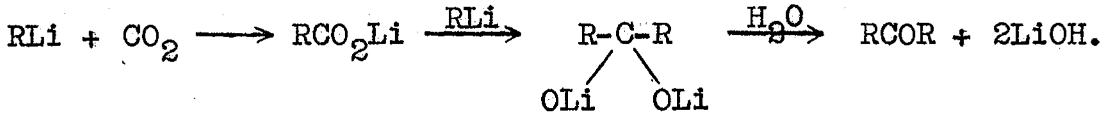
The aqueous layer was acidified and extracted with ether. A test on a neutr~~on~~al portion of the solution with calcium chloride showed the absence of oxalate (p.p.115-6). The dried ether extract was then distilled. Only a trace of liquid boiling at about 176°C. (n-valeric acid, b.pt. 176°C.) was observed. No other material could be extracted from the aqueou solution. This showed that only a small amount of n-butyl lithium, as such, was converted to n-valeric acid.

The ether/chloroform mixture was concentrated by distillation under nitrogen. Residual volatile matter at about .01 m.m. was condensed into a trap cooled in a solid carbon dioxide acetone mixture. This liquid was distilled unde nitrogen leaving behind about 1 c.c. of liquid (A), with a pleasant odour. Tests on samples of the residual red liquid (31.7 gms.) showed that it was miscible with benzene (and ether) but not in absolute alcohol. This would be expected of a di-alkyltin compound, in this case di-n-butyltin. Colourless solid was also left when a sample of the red liquid was allowed to stand in air. Analysis of tin in a sample of red liquid, by the volumetric method (page 97), give a value of 35.60%, which accounted for all the tin used in the reaction.

As the red solution was suspected to contain di-n-butyltin, an attempt was made to separate it as such. A sample (4 c.c.'s) was shaken with absolute alcohol when about 3 c.c.'s dissolved. The alcohol layer was removed by pipette and the residual liquid was shaken with more alcohol, which was again removed. At this stage the residual red liquid had become very viscous. This liquid was then run into a weighed flask, under nitrogen, and then the flask was pumped down to a hard vacuum (with a mercury diffusion pump), for about 2½ hours to remove residual volatile matter. The flask was reweighed after refilling with nitrogen. The tin in the sample was then estimated volumetrically (43.80%). The percentage of tin in di-n-butyltin is 51.0%. Although the tin content was low for di-n-butyltin it was noticeable that the percentage of tin had increased markedly suggesting the initial presence of material other than di-n-butyltin.

A small amount of liquid remained when the alcohol extract from the red liquid was distilled. This was combined with the liquid A and distilled at 2.7 m.m.'s, when a fraction (0.9 gm.) boiling at 50°C. was collected. This liquid which was believed to be an ester was shown, however, to contain no ester as no hydrolysis occurred on warming with alcoholic potassium hydroxide.

It had been reported that carbonation of alkyl lithium compounds with carbon dioxide, especially where the alkyl lithium was in excess, led to formation of a ketone,[20-22]



$$RLi + CO_2 \longrightarrow RCO_2Li \xrightarrow{RLi} R-\underset{OLi\quad OLi}{C}-R \xrightarrow{H_2O} RCOR + 2LiOH.$$

If this had occurred the ketone would be di-*n*-butyl ketone, boiling point 185-7°C., which would correspond approximately to a boiling point of 50°C. at 2.7 m.m.'s. As the liquid (b.pt. 50°C./2.7 m.m.'s) had been used the red liquid was pumped down to a hard vacuum for 3 hours and left overnight to condense all volatile matter into a trap cooled in liquid nitrogen. On distilling the liquid collected, most of the liquid proved to be chloroform, a small amount of liquid (0.7 gms.) boiling point 185°C. was collected; this afforded a semi-carbazone m.p. 89°C. (di-*n*-butyl ketone semicarbazone, m.pt. 90°C.), which confirmed the formation of di-*n*-butyl ketone. Assuming the equilibrium,

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li,$$

to occur, the amount of *n*-butyl lithium accounted for as di-*n*-butyl ketone (1.6 gms.) was 37%.

A sample of the red liquid (2 c.c.'s) was heated, under nitrogen, to about 70°C. with an excess of *n*-butyl-iodide until the solution became colourless (3 days). Then the reaction mixture was pumped to about 0.5 m.m. to remove excess *n*-butyl iodide (b.pt. 131°C. at atmospheric pressure) and the residual liquid was distilled at 10 m.m.'s, liquid distilling up to 65°C. being collected. No higher boiling fractions corresponding to tri-n-butyltin iodide (b.pt. 172°C./10 m.m.'s) were obtained. However, a solid acetate was obtained from the liquid which distilled at 10 m.m.'s by treatment respectively with alkali and acetic acid (page100); this melted at about 76°C. after repeated recrystallisation (tri-n-butyltin acetate, m.pt. 84°C.). An attempt to show that the solid was impure tri-n-butyltin acetate by means of a mixed melting point with authentic tri-n-butyltin acetate was unsuccessful, since there was no apparent increase in the melting point of the mixture.

The reaction between tri-n-butyltin lithium and carbon dioxide was repeated.

In this reaction n-butyl lithium was prepared in n-pentane. n-Butyl lithium in such a solvent can be kept for extended periods without decrease of strength.[23] Lithium (10.5 gms., 1.5 mole) was converted to shot and stirred, under nitrogen, with n-pentane (250 c.c.'s). A solution of n-butyl chloride (60.1 gms., 0.65 mole) in n-pentane (500 c.c.'s) was added at such a rate to keep the solution refluxing gently. Occasional cooling with cold water was necessary. The solution was stirred for 1 hour after addition of n-butyl chloride was completed and then the mixture was left to stand overnight under nitrogen.

The solution was then blown over into another flask leaving most of the lithium chloride behind. Then the solution was concentrated somewhat by distilling off some *n*-pentane (about 250 c.c.'s), and the cooled solution was filtered under nitrogen to remove residual solid. Another advantage of this method is that the halide formed (lithium chloride in this case) is insoluble in the pentane; there is a marked solubility in ether. The strength of the solution can usually be estimated by a single titration as there should be virtually no lithium present other than as *n*-butyl lithium. As, however, the final solution was somewhat grey in colour, the strength of the solution was estimated by the method used for *n*-butyl lithium in ether.[17] The yield of *n*-butyl lithium indicated by titration was 47.9%. By this method it was hoped to prepare a stock solution of *n*-butyl lithium which could be kept and used for reactions as required.

The solution of *n*-butyl lithium was then added to stannous chloride (17.7 gms., .093 mole) in ether (100 c.c.'s) until the colour test with *p*-bromdimethylaniline became positive.[18] As in the previous reaction the colour test became positive before the calculated volume of *n*-butyl lithium solution had been added. The tri-*n*-butyltin lithium mixture was then run onto a slurry of solid carbon dioxide and ether. By carbonation in this manner, where the carbon dioxide was in excess, it was hoped to obtain some *n*-valeric acid from *n*-butyl lithium. When addition was complete the mixture was left to warm to room temperature.

It was noted that if the blank in the estimation of n-butyl lithium was neglected the yield became 54.8%. Assuming that 17.7 gms. of stannous chloride (.093 mole) were equivalent to the volume of n-butyl lithium used and then calculating the total amount of n-butyl lithium in the original solution, the yield of n-butyl lithium became 52.5%. As the error was only 2.3% it appeared that the blank estimation with benzyl chloride, at least in n-pentane, was misleading.

The reaction mixture was stirred, under nitrogen, with water (150 c.c.'s) to remove lithium salts and any lithium valerate. As solid was present the whole mixture was filtered, under nitrogen. The two layers were then separated.

The aqueous layer was tested for carbonate (lithium carbonate), which was found to be present, and oxalate, which was found to be absent (Walker and Scott[21] reported formation of carbonates when lithium alkyls react with carbon dioxide to give ketones). The solid filtered from the two phases was also lithium carbonate. The aqueous solution was made acid, extracted with ether, the ether extract separated, dried over magnesium sulphate, and distilled. A small residue remained. This was distilled from a smaller apparatus, and a fraction boiling at 185-7° C. was collected, mainly at 186.5°C. (n-valeric acid, b.pt. 186-7°C.). The liquid collected weighed 3.6 gms. The equivalents found by titration of weighed quantities of this liquid with 0.1N potassium hydroxide were 106.1 and 105.5 (theoretical value for n-valeric acid 102.3). Another sample of the liquid was heated with p-toluidine for 2 hours at 160°C. After working up a p-toluidide was obtained which melted at 71-71.5°C. (Beilstein reports the melting point of the p-toluidide of n-valeric acid as 72°C.). The presence of n-valeric acid was confirmed in 37.8% yield (based on the equation):-

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li.$$

The ether and pentane mixture was concentrated by distillation, under nitrogen, leaving a deep red solution behind. The residual solution was then pumped down to a hard vacuum, and volatile liquid collected in a trap cooled in liquid nitrogen. The deep red liquid, non-volatile at room temperature, weighed 19.8 gms. This liquid was shaken with methyl alcohol to extract any di-n-butyl ketone present. The methyl alcohol extract was removed by pipette and then the red liquid was pumped to remove any residual methyl alcohol. 1.6 gms. of liquid was extracted (loss in weight of red liquid).

An attempt to isolate di-n-butyl ketone from the methyl alcohol extract was not successful as no steady boiling point was observed. A fraction b.pt. 185-195°C. collected weighed 2.1 gms. A semicarbazone obtained from a sample of this liquid melted at 87.5-88°C. Further recrystallisation did not increase the melting point (di-n-butylketone semicarbazone, m.pt. 90°C.). An authentic specimen prepared from known di-n-butylketone melted at 89.5-90°C. A mixed melting point was 89°C. This confirmed the presence of di-n-butylketone. An indication of the yield of ketone from the reaction was obtained by weighing the semicarbazone (0.9 g.) obtained from a weighed amount of the liquid fraction (0.9 g.). From this the yield of di-n-butylketone was calculated to be 22.6%.

The deep red liquid was dissolved in cyclo-hexane and left to oxidise in the air. As the reaction was slow 4% hydrogen peroxide solution was added and the solution was shaken and left until it was almost colourless. The mixture was then shaken with concentrated hydrochloric acid. Then the dried cyclo-hexane layer was distilled to remove the solvent. On chilling the residual liquid (A) solid (2.7 gms.) was obtained. After purification by recrystallisation from n-pentane and sublimation the melting point of the solid was 39-39.5°C. A sample of authentic di-n-butyltin dichloride was purified similarly and melted at 39-39.5°C. The mixed melting point was unchanged and confirmed the presence of di-n-butyltin dichloride. This confirmed the presence of di-n-butyltin radical[24],

$$(\underline{n}\text{-}C_4H_9)_2Sn + O_2 \longrightarrow (\underline{n}\text{-}C_4H_9)_2SnO \xrightarrow{HCl} (\underline{n}\text{-}C_4H_9)_2SnCl_2.$$

The liquid (A) was distilled at ~.01 m.m. but the distilled liquid did not solidify. Practically all the liquid (A) distilled. Another amount of dichloride (0.8 gms.) was, however, obtained by chilling the liquid (A) and filtering while cold. The total amount of di-n-butyltin dichloride obtained was 3.5 gms. A small sample of the residual liquid (A) was dissolved in ether and shaken with sodium hydroxide solution. The residue left after distillation of ether from the ether layer was heated to 125°C. with glacial acetic acid. After purification an acetate was obtained which melted at 84°C. An authentic specimen of tri-n-butyltin acetate[19] melted at 84.5°C. The mixed melting point was 84.5°C. The presence of the tri-n-butyltin radical was thus confirmed.

Another 3.7 gms. of chloride mixture was obtained by concentrating the aqueous hydrochloric acid phase. The total weight of chloride mixture was 12.9 gms. As the separation of the chlorides is difficult no attempt was made to separate the mixture further. The 12.9 gms. of chloride mixture obtained represented about 44% of the tin used in the reaction.

In the reaction between tri-n-butyltin lithium and carbon dioxide assuming the equilibrium,

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li,$$

to occur 60.4% of the n-butyl lithium was recovered as a mixture of n-valeric acid and di-n-butylketone. About 44%

of the tin used in the reaction was recovered as a mixture of tri-n-butyltin chloride and di-n-butyltin dichloride.

Reaction with β-Phenylethyl Bromide

Before the reaction between β-phenylethyl bromide and tri-n-butyltin lithium was carried out a sample of β-phenylethyltri-n-butyltin was synthesised as this compound has not previously been reported and was expected to be one of the main products of reaction.

Tri-n-butyltin chloride was prepared from the oxide:-

$$\left[(\underline{n}\text{-}C_4H_9)_3Sn\right]_2O + 2HCl = 2(\underline{n}\text{-}C_4H_9)_3SnCl + H_2O.$$

Tri-n-butyltin oxide (60 g., 0.1 mole) was shaken with concentrated hydrochloric acid (100 c.c.'s., ~ 1 mole), the solution extracted with n-pentane, the n-pentane extract washed with a small amount of water, dried over magnesium sulphate and the n-pentane removed by distillation. The residual liquid was distilled at 9 m.m.'s and a fraction b.pt. 140-151°C. was collected (40 g., 0.122 mole, 61% yield).[36] As this liquid was slightly cloudy it was redistilled before use and the main fraction b.pt. 151-152°C./9 m.m. was collected.

β-Phenylethylmagnesium bromide was prepared by addition of β-phenylethylbromide (17.5 g., 0.095 mole) in ether (60 c.c.'s) to magnesium (2.5 g., 0.103 mole) and ether (20 c.c.'s) under N_2. A solution of tri-n-butyltin chloride (15.3 g.,

.047 mole) in ether (20 c.c.'s) was then added over 20 minutes and then the reaction mixture was refluxed for another 50 minutes. After working up a liquid b.pt. 153-163°C./1.9-2^+ m.m.'s was collected. On refractionation at 1.6 m.m.'s this liquid boiled at 145-149 °C. (11.1 g.) the fraction b.pt. 148-149°C./1.6 m.m.'s being retained for analysis:-

found:- C = 61.62%, H = 9.36%.

The liquid b.pt. 145-149°C./1.6 m.m.'s was therefore again fractionated, a fraction b.pt. 148°C./1.5 m.m. being used for analysis:-

	% C	%H	%Sn
Sample	61.16	9.04	29.86*
Calc. for β-C_8H_9-Bu_3Sn	60.78	9.18	30.04

* volumetrically page 97.

The preparation of β-phenylethyltri-*n*-butyltin was confirmed. The yield (liq. b.pt. 145-149°C/1.6 m.m.'s) was 60%.

A large scale preparation of *n*-butyl lithium was carried out in *n*-pentane so that the product could be stored and used for various reactions. A solution of *n*-butyl chloride (60.1 g., 0.65 mole) in *n*-pentane (200 c.c.'s) was added to a stirred suspension of lithium shot (~10.5 g., ~ 1.5 mole) in *n*-pentane (250 c.c.'s) under nitrogen. When reaction started the butyl chloride was further diluted with n-pentane (300 c.c.'s). After working up in the usual way and concentrating by distillation, under nitrogen, a 72% yield of n-butyl lithium was obtained (final volume of solution 330 c.c.'s).

$$\beta\text{-}C_6H_5CH_2CH_2Br + (n\text{-}C_4H_9)_3SnLi = \beta\text{-}C_6H_5CH_2CH_2(n\text{-}C_4H_9)_3Sn + LiBr.$$

The n-butyl lithium solution, prepared above, was added to stannous chloride (13.3 g., 0.07 mole) in ether (150 c.c.'s), under nitrogen, at -10 to -20°C. until the colour test[18] with p-bromdimethylaniline was positive (116 c.c.'s of n-butyl lithium solution). The calculated volume of n-butyl lithium solution required was 113 c.c.'s. A solution of β-phenylethyl bromide (13 g., 0.073 mole) in ether (100 c.c.'s) was added to the tri-n-butyltin lithium solution at -10 to -20°C. over ~ 30 minutes. The deep red-brown colour of the tri-n-butyltin lithium solution gradually became a pale yellow. Then the reaction mixture was allowed to warm slowly to room temperature and was refluxed gently for 2 hours, but no further change in colour occurred. After this stage working up was carried out in air as the products of reaction were not expected to be air-sensitive.

The reaction mixture was stirred with an ammonium chloride solution and the ether/n-pentane layer separated. This was a very pale yellow in colour and rapidly became almost colourless.

The aqueous phase was colourless with a small amount of white solid present. A small amount of dark greyish solid was also collected from the aqueous phase. After drying over magnesium sulphate the ether/n-pentane mixture was concentrated by distillation. An attempt to fractionate the residual liquid using a vacuum-jacketed column at 1.4 m.m.'s was then made. An initial fraction b.pt. 60-64°C./1.4 m.m.'s (1.5 g.) was obtained but no liquid corresponding to β-phenylethyl-tri-n-butyltin (b.pt. 148°C./1.5 m.m.'s), although the oilbath was raised to 180°C. The lower fraction was probably unreacted β-phenylethylbromide (b.pt. 94°C./11 m.m.'s). An attempt was then made to collect higher boiling fractions without a column but no liquid distilled when the oilbath was again raised to 180°C. However, a liquid fraction (13.4 g.) b.pt. 125-160°C./1.4 m.m.'s was collected when the flask was heated with a naked flame. A sample of this liquid (6.8 g.) was redistilled at 1.4 m.m.'s using a small vacuum-jacketed column the following fractions being collected:-

1) up to 112°C./1.4 m.m.'s; oilbath ~190°C.
2) 113-127°C./1.4 m.m.'s
3) 127°C./1.4 m.m.'s; oilbath ~220 °C.

More liquid was collected at a much lower pressure:-

4) 93-108°C./ .01 m.m.'s
5) 108-120°C./ .001 m.m.'s; oilbath ~230°C.
6) 125-149°C. less than .001 m.m.'s; oilbath ~ 300°C.

Fractions 1), 2) and 3) were redistilled at 1.5 m.m.'s:-

1)^1 up to 109°C./1.5 m.m.'s) ; oilbath $\sim$170°C.
2)^1 109-113°C./1.5 m.m.'s) + 6)^1, 1 g.
3)^1 113-117°C./1.5 m.m.'s)
4)^1 117-119°C./1.5 m.m.'s) ; oilbath $\sim$180°C.
5)^1 119-120°C./1.5 m.m.'s) 1.1 g.
6)^1 119-121°C./1.5 m.m.'s ; oilbath $\sim$185°C.

Fractions 4), 5) and 6) were redistilled, in vacuo:-

1)^2 up to 100°C.) ; oilbath $\sim$190°C.
2)^2 100-113°C.) + 5)^2, 1 g. ; oilbath $\sim$200°C.
3)^2 113-116°C.) ; oilbath $\sim$200°C.
4)^2 116-117°C.) 1.6 g.
5)^2 117°C.↓

Fraction's 4)^1 and 5)^1 were refractionated at 1.5 m.m.'s and a middle fraction b.pt. 117-119°C. was collected for carbon and hydrogen analysis. Similarly fractions 3)^2 and 4)^2 were refractionated and a middle fraction b.pt. 117-119°C, in vacuo, was collected for carbon and hydrogen analysis.

The liquid b.pt. 117-119°C./1.5 m.m.'s gave the following analysis, carbon 57.23% and hydrogen 10.48%, and that distilling at 117-119°C, in vacuo, carbon 63.46% and hydrogen 9.26%. The corresponding values for

β-phenylethyltri-n-butyltin and tetra-n-butyltin are as shown:-

	%C	%H
β-$C_6H_5CH_2CH_2(n\text{-}C_4H_9)_3Sn$	60.78	9.18
$(n\text{-}C_4H_9)_4Sn$	55.35	10.45

The qualitative tin test on these fractions was positive.

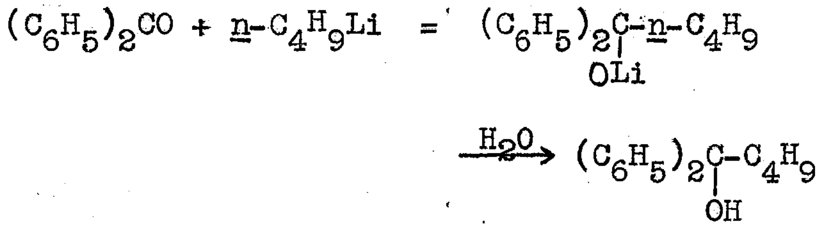
As the separation of any pure β-phenylethyltri-n-butyltin (or tetra-n-butyltin) did not appear feasible by distillation in this reaction an attempt was made to show the presence of the β-phenylethyl radical in the higher boiling fraction (~120°C. *in vacuo*). A sample of the combined fractions 1)^2 and 2)^2 was treated with 4% bromine in carbon tetrachloride until the solution was permanently red. Carbon tetrachloride was then removed and neat bromine added and then the excess bromine and any n-butyl bromide was removed by heating to *ca*. 120°C; the residue was dissolved in ether and the solution shaken with aqueous potassium hydroxide solution to remove tin (*e.g.* as organo-tin oxides *etc*.). After washing and drying the ether solution ether was removed by distillation. The residual liquid was then distilled in a micro-distillation apparatus at 9 m.m.'s and an oil-bath temperature of 100°C. The colourless distillate solidified on cooling. As β-phenylethyl bromide is a liquid (b.pt. 98°C./12 m.m.'s), and the tri-n-butyltin halides are liquids it was suspected that the solid might be an organo-tin dibromide. An attempt was therefore made to prepare an "oxine" derivative (pp. 101) from the solid but this was unsuccessful.

As it had not proved possible to separate any single component from the reaction products this reaction was abandoned.

Reaction with Benzophenone

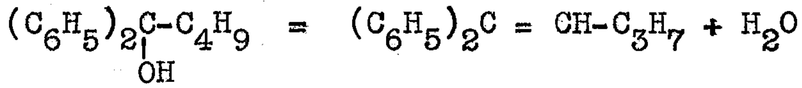
a) $(n\text{-}C_4H_9)_3SnLi \rightleftharpoons (n\text{-}C_4H_9)_2Sn + n\text{-}C_4H_9Li$

b)



$$(C_6H_5)_2CO + n\text{-}C_4H_9Li = (C_6H_5)_2\underset{OLi}{C}\text{-}n\text{-}C_4H_9 \xrightarrow{H_2O} (C_6H_5)_2\underset{OH}{C}\text{-}C_4H_9$$

c)



$$(C_6H_5)_2\underset{OH}{C}\text{-}C_4H_9 = (C_6H_5)_2C = CH\text{-}C_3H_7 + H_2O$$

n-Butyl lithium in n-pentane, prepared prior to the previous reaction, was added to stannous chloride (13.3 g., 0.07 mole) in ether (150 c.c.'s) until the colour test with p-bromdimethylaniline was positive.[18] This occurred when the theoretical volume of n-butyl lithium had been added (113 c.c.'s). A solution of benzophenone (12.8 g., 0.07 mole) in ether (100 c.c.'s) was added to the tri-n-butyltin lithium solution at -15°C. over 25 minutes. The solution appeared to darken. After the reaction mixture had warmed to room temperature it was stirred for another two hours. On standing unstirred, the supernatant liquid was olive green in colour. Orange solid was present at the bottom of the flask.

After standing for two days under nitrogen the olive green colour had disappeared leaving an orange-red solution with orange solid present.

As di-n-butyltin was expected to be formed in this reaction and would interfere with the separation of other reaction products a stream of oxygen was bubbled through the solution. In this way di-n-butyltin would form the insoluble oxide which could be removed by filtration. After bubbling oxygen through the solution for 24 hours the reaction mixture was shaken with ammonium chloride solution containing hydrogen peroxide (10 vol., 20 c.c.'s). In order to remove solid from the resultant liquid phases the whole mixture was filtered through "hyflo super cel", and the ether/n-pentane layer collected. The solid on the "hyflo super cel" was then washed with 2N hydrochloric acid to decompose any lithium carbinol derivative present and the acid washings extracted with ether, which was added to the ether/n-pentane mixture collected previously. After drying over magnesium sulphate, ether and n-pentane were removed by distillation. A slightly cloudy golden yellow liquid remained.

The "hyflo super cel" which was expected to contain di-n-butyltin oxide was treated with warm concentrated hydrochloric acid and the mixture extracted with n-pentane. However, no di-n-butyltin dichloride was left after removal of n-pentane. In view of this the "hyflo super cel" was retreated with concentrated hydrochloric acid and the mixture heated for 30 minutes. This time 2.8 g. of brownish solid was extracted by n-pentane. The solid was shown to be di-n-butyltin dichloride by subliming, in vacuo, after recrystallising from n-pentane, m.pt. 33-36°C. (di-n-butyltin dichloride, m.pt. 40.5°C.). A sample of the sublimed solid was converted to the "oxine" derivative (pp. 101) and recrystallised in turn from ethanol and petroleum ether (80-100°) m.pt. 153-153.5°C. An authentic sample of the di-n-butyltin oxine derivative melted at 154-154.5°C. The mixed m.pt. was 153-154°C. An attempt to obtain more di-n-butyltin dichloride from the "hyflo super cel" by treatment with acid followed by extraction with n-pentane was unsuccessful.

The dichloride extracted, 2.8 g., represented 13.2% of the tin used in the reaction.

The colour of the liquid left from the ether/n-pentane solution remained unchanged on standing in air or treatment with hydrogen peroxide, i.e., the colour was not apparently due to di-n-butyltin. This liquid weighed 17.9 g. On distillation at 1 m.m. the fractions b.pt. 119-127°C. (5.7 g., pale yellow in colour) and 127-135°C. (2.9 g., yellow in colour) were collected. The liquid, which remained undistilled, was a deep red-brown in colour, the colour becoming progressively darker as distillation continued. A very viscous liquid was eventually left undistilled. Further purification of the liquid distilled was then attempted using a small vacuum-jacketed column.

First fractionation[d] of liquid b.pt. 119-127°C./1 m.m.:-

1)^1 up to 104°C./1 m.m., plus liquid undistilled in second fractionation[e], 0.6 g.

2)^1 105-106°C/1 m.m.) , oilbath 180°C.
3)^1 106-110°C/1 m.m.) 3 g.
4)1 110-111°C/1 m.m.)

5)^1 111-123°C/1 m.m., 1.3 g., oilbath 200°C.

Undistilled liquid, which was viscous and yellow in colour, was added to the fraction b.pt. 127-135°C./1 m.m.

The fractions 2)^1 to 4)^1 were redistilled:-[e]

1)^2 up to 107°C./1 m.m., 0.8 g.

2)^2 107-108°C./1 m.m., 0.6 g.

3)^2 108-109°C./1 m.m., 0.8 g.

The qualitative tin test on these fractions was only positive with fractions 2)^2 and 3)^2.

A carbon and hydrogen analysis on 3)^2 gave the values, carbon 64.82% and hydrogen 8.68%. The most probable tin compound formed in the reaction and boiling in this range would be tetra-n-butyltin, (b.p.t.'s 127°/1.7 m.m.,109°/0.5 m.m. which contains 55.35% carbon and 10.45% hydrogen. However, the compound, $(C_6H_5)_2C{=}CH{-}C_3H_7$, another expected product of reaction has a similar boiling point 125-126°C./1 m.m. The presence of the latter compound in tetra-n-butyltin as impurity would also account for the increase of carbon content and decrease of hydrogen in tetra-n-butyltin. Thus it seemed probable that the liquid consisted of a mixture of tetra-n-butyltin and the compound $(C_6H_5)_2C{=}CH{-}C_3H_7$.

The liquid b.pt. 127-135°C/1 m.m. and liquid undistilled from the lower boiling fraction was redistilled, using the vacuum-jacketed column, in vacuo:-

1) up to 100°C., 1.8 g., oilbath ~ 190°C.
2) 100-110°C./1 , 1.2 g., oilbath ~ 230°C.

No steady boiling point was observed. The qualitative tin test applied to 1) was negative. However, both fractions yielded a 2:4-dinitrophenylhydrazone, although neither fraction crystallised after cooling in an acetone/carbon dioxide bath. The 2:4-dinitrophenylhydrazone melted at 235.5-237°C; a 2:4-dinitrophenylhydrazone prepared from benzophenone melted at 236-237°C. The mixed melting point was 235.5-236.5°C. Assuming the fractions distilled to be benzophenone (3 g.), this accounted for ~23% of the benzophenone used in the reaction.

The red viscous liquid (5.6 g.), which was undistilled at 1 m.m., remained unchanged in colour after standing in air and was soluble in alcohol, indicating the absence of di-n-butyltin, although the qualitative tin test was positive. This liquid did not appear to contain benzophenone as no 2:4-dinitrophenylhydrazone was obtained.

As the fractions $2)^2$ and $3)^2$ were suspected to contain some, $(C_6H_5)_2C = CH-C_3H_7$, an attempt was made to obtain a qualitative indication of the presence of the compound. The combined fractions were dissolved in acetone and oxidised with a saturated solution of potassium permanganate in acetone by gentle warming. Acetone was then distilled off and the residue was extracted with ether, which was then dried over magnesium sulphate. The residue left after removal of ether was used in an attempt to prepare a 2:4-dinitrophenylhydrazone. No derivative was formed. In the presence of $(C_6H_5)_2C = CH-C_3H_7$ breakdown to benzophenone was expected.

Thus from the reaction between tri-n-butyltin lithium and benzophenone approximately 13% of the tin was recovered as di-n-butyltin dichloride and approximately 23% of impure benzophenone recovered. A small amount of liquid which probably contained impure tetra-n-butyltin (decomposition of di-n-butyltin) was also formed and a red viscous liquid containing tin which did not appear to be air-sensitive.

Reaction with Water

a) $3\underline{n}C_4H_9Li + SnCl_2 = (\underline{n}-C_4H_9)_3SnLi + 2LiCl.$

b) $(\underline{n}-C_4H_9)_3SnLi \rightleftharpoons (\underline{n}-C_4H_9)_2Sn + (\underline{n}-C_4H_9)Li.$

c) $\underline{n}-C_4H_9Li + H_2O = \underline{n}-C_4H_{10} + LiOH.$

d) $2(\underline{n}-C_4H_9)_3SnLi + 2H_2O = 2(\underline{n}-C_4H_9)_3Sn^{\bullet} + 2LiOH + H_2.$

e) $2(\underline{n}-C_4H_9)_3Sn^{\bullet} = (\underline{n}-C_4H_9)_3SnSn(\underline{n}-C_4H_9)_3.$

As n-butane was expected to be formed in this reaction the n-butyl lithium was prepared in ether to facilitate separation from the solvent (i.e. separation of ~~n-pentane~~ n-butane from ether rather than a mixture of ether and n-pentane). n-Butyl lithium was prepared from n-butyl bromide (51.4 g., 0.375 mole) in ether (90 c.c.'s) and lithium (7.5 g., over 1 mole) in ether (100 c.c.'s). The yield found by titration in the usual way was 80.7%. The solution of n-butyl lithium so prepared was then added to stannous chloride (16.8 g., 0.089 mole) in ether (100 c.c.'s) until the colour test[18] with p-bromdimethylaniline was positive (180 c.c.'s of n-butyl lithium solution). A mixture of tetrahydrofuran (100 c.c.'s) and water (100 c.c.'s) was added slowly to the stirred solution at -10 to -20°C. There was no apparent change in colour. Volatile products were collected in traps connected to the reaction vessel via the water-condenser, the first cooled in a solid carbon dioxide/acetone mixture and the second cooled by liquid nitrogen. When addition of the aqueous tetrahydrofuran was completed the reaction mixture was allowed to warm to room temperature and was then refluxed gently for 15 minutes to ensure complete removal of n-butane. The residual mixture was a deep brown in colour. Liquid collected in the trap cooled by acetone/solid carbon dioxide was transferred to the other trap by gentle heating. The material in the trap was then transferred to a vacuum system.

The liquid in the vacuum apparatus was allowed to evaporate up a short vacuum-jacketed helices column cooled at the top to -70°C. and connected to two traps cooled by toluene slush baths (-95°C.) and finally to a trap cooled in liquid nitrogen. When all the liquid had passed through the helices column liquid was found in the first trap cooled by a toluene slush bath and solid in the trap cooled by liquid nitrogen. The first trap cooled by the toluene slurry was then removed and the liquid was allowed to pass into the second trap cooled by a toluene slurry, while allowing any n-butane to pass into the final trap cooled in liquid nitrogen. The vapour pressure of the liquid collected by the toluene trap was ca. 1-2 m.m.'s at the temperature of a solid carbon dioxide/acetone bath (v.p. of ether 0.7 m.m. at -78°C.). The more volatile material was measured in a gas volume measuring bulb and was found to be 111.4 N c.c.'s. The vapour pressure of this material however was found to be 166 m.m.'s at -33.5°C. while that reported for n-butane is 181 m.m.'s. In view of this the material was refractionated using the same system as before. The amount of gas then measured was 69.2 N c.c.'s. As the volume of the measuring bulb was too large to enable a vapour pressure measurement being made at -35.5°C., the vapour pressure at -79.5°C. using a solid carbon dioxide/acetone bath was determined and found to be 12.6 m.m.'s (v.p. of n-butane 9.1 m.m.'s at -78.5°C.).

The aqueous phase was separated from the ether/tetrahydrofuran mixture, dried over magnesium sulphate, filtered, and distilled under nitrogen. When the temperature of the distilling liquid rose to ~ 40°C. heating was discontinued as grey solid started to form in the red liquid. A small amount of grey solid (tin) collected in the aqueous phase weighed 0.1 g. More solvent was removed from the red liquid by evacuating to ca. 0.1 m.m. and collecting volatile material in a trap cooled in carbon dioxide/acetone. Finally the trap was cooled in liquid nitrogen and the pressure reduced to ca. 0.005 m.m. for 45 minutes and the red liquid heated to 50°C. The liquid collected was coloured due to bumping over of some of the residual liquid. The collected liquid was then distilled under nitrogen to remove ether and tetrahydrofuran, 8.1 g. of liquid remained. An attempt to distil this liquid at 1.7 m.m.'s was unsuccessful, a very small amount of liquid b.pt. ~ 127°C. was observed ($(\underline{n}\text{-}C_4H_9)_4Sn$, b.pt. 127°C./1.7 m.m.'s), the distilling flask being heated to ~ 170°C. Solvent (mainly tetrahydrofuran) collected in a trap cooled in liquid nitrogen connected to the distillation apparatus. The liquid left (4 g.) was red in colour. This liquid was added to the other red liquid, which was left after pumping, in vacuo, at 50°C. The total weight of red liquid was 16.4 g. On standing in air a sample of the red liquid left a white solid, indicating the presence of di-n-butyltin. A sample of this white solid was dissolved in warm concentrated hydrochloric acid, and the cool solution extracted with n-pentane. The residue left after removal of n-pentane was used to prepare an oxine derivative (page 101).

The yellow solid obtained after crystallising from ethanol and petroleum ether (80-100°) melted at 153-154°C. A mixed melting point with authentic di-n-butyltin oxine derivative (m.pt. 154 ± °C) was 153-154°C. Another sample of the white solid was dissolved in glacial acetic acid and heated to 125°C. for 30 minutes. After removal of excess acetic acid the solid remaining was recrystallised from petroleum ether (60-80°), m.pt. 84-84.5°C. A mixed melting point with authentic tri-n-butyltin acetate (m.pt. 84.5°C.)was 84-84.5°C. These two tests confirmed the presence of the tri-n-butyltin radical in the red liquid.

As the amount of n-butane formed in this reaction was small (~100 N c.c.'s of gas instead of ~ 2,000 N c.c.'s in accordance with equation c) the reaction was repeated using a more gas-tight system. A copper oxide furnace was also coupled to the system to convert any hydrogen, formed by reactions d) and e), to water, which was to be estimated gravimetrically after absorbing by "anhydrone".

n-Butyl lithium was prepared from n-butyl bromide (51.4 g., 0.375 mole) in ether (90 c.c.'s) and lithium (7.5 g., over 1 mole) stirred in ether (100 c.c.'s). The yield of n-butyl lithium was 79.5%. Tri-n-butyltin lithium was then prepared by adding the n-butyl lithium to stannous chloride (17.1 g., 0.091 mole) in ether (100 c.c.'s) until the colour test with p-bromdimethylaniline was positive.[18] A small amount of stannous chloride was then added to the mixture and caused the test to become negative. In this way an excess of n-butyl lithium, which would give rise to formation of n-butane on hydrolysis, was avoided. A set of traps, connected by pressure tubing to the reaction vessel in order to have a gas-tight system, were cooled, the first in a solid carbon dioxide/acetone mixture and the other two in liquid nitrogen. The apparatus was purged with nitrogen to remove any ether vapour beyond the traps and then the apparatus was connected to a copper oxide furnace (20 cms. long and 1.5 cms. diameter) and two previously weighed U-tubes filled with "anhydrone". The furnace was then heated by means of two fish-tail burners and a mixture of water (100 c.c.'s) and tetrahydrofuran (90 c.c.'s) was added slowly to the reaction vessel, which was swirled by hand; a steady evolution of gas was observed. When all the aqueous tetrahydrofuran had been added nitrogen was passed through the system for three hours to ensure complete passage of hydrogen through the furnace, after which the U-tubes were isolated from the reaction system. The reaction vessel was then heated to reflux temperature for ca. 30 minutes to ensure removal of any n-butane dissolved in the ether/tetrahydrofuran mixture. About 50 c.c.'s of ether was collected in the solid carbon dioxide/acetone trap and a small amount of water. This was heated and about half the ether transferred to the final trap cooled in liquid nitrogen. In this way any n-butane dissolved in the ether would be collected in the trap cooled in liquid nitrogen.

The material collected in the liquid nitrogen trap was then transferred to a vacuum apparatus. Initial fractionation was carried out as before using the helices column, two toluene slush baths and a liquid nitrogen trap. When, however, all the liquid had been removed from the helices column all the cooling baths were removed one trap foreward. Thus liquid collected in the first toluene trap now redistilled into the first toluene trap again and the material frozen out in the liquid nitrogen trap was allowed to distil from the trap, this time cooled by a toluene trap, into the liquid nitrogen trap again. In this manner a better separation of ether and n-butane was anticipated. The vapour pressure of the liquid retained by the toluene traps was 2-3 m.m.'s when cooled by a solid carbon dioxide/acetone bath (vp. of ether 0.7 m.m. at -78.5°C.). The more volatile component was measured as gas (154.6 N-c.c.'s, 0.0069 moles). The vapour pressure of the product was then measured when cooled by an acetone/solid carbon dioxide bath and by acetone at -32.5°C, the values being 9.8 m.m.'s and 180.1 m.m.'s respectively. The corresponding values for n-butane at -78.5°C. and -33.4°C are 9.1 m.m.'s and 181.0 m.m.'s respectively. Formation of n-butane was indicated in 7.6% yield based on the equations:-

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li.$$

$$\underline{n}\text{-}C_4H_9Li + H_2O = \underline{n}\text{-}C_4H_{10} + LiOH.$$

The amount of water collected in the first U-tube filled with "anhydrone" was 0.260 g., none collected in the second U-tube. The amount of water collected represented 31.7% of the theoretical amount of hydrogen formed by the reactions d), and e). This value would be high if any metallic lithium was present in the n-butyl lithium solution.

The red ether/tetrahydrofuran layer was separated from the aqueous layer, the ether layer being dried over magnesium sulphate and kept under nitrogen. Grey solid formed in this reaction on hydrolysis as in the previous one. After filtration under nitrogen the red ethereal layer was concentrated by distillation. Residual volatile liquid was removed, in vacuo, using a nitrogen leak to prevent bumping. The liquid was maintained at ca. 80°C. for 2½ hours. On distillation of the liquid collected in the liquid nitrogen trap most boiled at 64-66°C. (tetrahydrofuran), about 1 c.c. of liquid remained. The residue (0.7 g.) was distilled at 1.3 m.m.'s using a micro-distillation apparatus and a middle fraction b.pt. 90°C. (oilbath temperature) was collected. A small amount of viscous material remained undistilled. A carbon/hydrogen analysis of this liquid gave the results 76.4% carbon and 14.0% hydrogen. These values did not fit any expected product. A sample of the red liquid remaining after pumping, in vacuo, was analysed for tin (35.5%). The weight of red liquid was 18.4 g. The results of the analysis were not consistent with a mixture of di-n-butyltin (51.0% tin) and hexa-n-butylditin (40.9% tin) or an organo-tin chain compound. The amount of tin in the red liquid represented 60.5% of that used in the reaction.

As the solution of tri-n-butyltin lithium had behaved in a complex manner with a variety of reagents, particularly with a simple reagent such as water, further experiments with it were abandoned.

(h) Reaction between Trimethyltin Bromide and Lithium

$$(CH_3)_3SnBr + 2Li = (CH_3)_3SnLi + LiBr$$

$$(CH_3)_3SnLi + (CH_3)_3SnBr = (CH_3)_3SnSn(CH_3)_3 + LiBr.$$

This reaction was designed particularly to show whether the greenish-yellow solution obtained by the reaction between lithium and trimethyltin bromide in tetrahydrofuran contained trimethyltin lithium.

Trimethyltin bromide (18.0 g., 0.074 mole) in tetrahydrofuran (30 c.c.'s) was added to lithium (~2.3 g., ~ 0.3 mole) stirred in tetrahydrofuran (60 c.c.'s) under nitrogen. The solution was maintained at ca. -20°C. The green solution produced was stirred for 20 minutes to complete the reaction and was then filtered through a glass-wool plug (in a rubber tube) into a graduated dropping funnel. 20 c.c.'s of solution were lost at this stage, the final solution amounted to 75 c.c.'s. On addition of the green solution to trimethyltin bromide (18.0 g., .074 mole) in tetrahydrofuran

(40 c.c.s) at -20°C. the green colour disappeared leaving an almost colourless solution. The solution was allowed to warm to room temperature and stirred for 1 hour.

An attempt to concentrate the solution by distillation was only partially successful as the solution became a deep red-brown in colour, indicating decomposition, when about 60 c.c.'s of tetrahydrofuran had distilled. Heating was discontinued at this stage. In view of the fact that heatin appeared to cause decomposition of the reaction mixture an attempt was made to remove residual solvent by evacuating the reaction vessel to 5 m.m.'s and condensing volatile liquid into a trap cooled by liquid nitrogen. However, only a small quantity of liquid was condensed. In view of this fact the reaction mixture was diluted with ether (150 c.c.'s) and stirred with 2N sodium hydroxide (250 c.c.'s) under nitrogen. A red solid was observed at this stage in the mixture. The aqueous layer was removed, and the ether layer, kept under nitrogen, was stirred with 2N sulphuric acid (250 c.c.'s) and the acid layer removed as before. (This procedure using alkali and acid had been shown previously to remove trimethyltin bromide completely from ether). The ether layer was then filtered under nitrogen and the small amount of red solid collected.

After drying over magnesium sulphate the ether solution was concentrated by distillation and pumping at <u>ca</u>. 3 m.m.'s. Finally the residual material was distilled at 5.2 m.m.'s, when liquid b.pt. 54-58°C. was collected (10 g.). A fraction of this liquid was purified by distillation through a short vacuum-jacketed column, b.pt. 49.5-50°C./4.5 m.m.'s (all the liquid b.pt. 54-58°C./5.2 m.m.'s on redistillation at 4.5 m.m.'s boiled at 49-50°C.). All the liquid collected crystallised on local cooling with a piece of solid carbon dioxide. The sample collected was then analysed for carbon, hydrogen and tin. (Found: C, 21.82; H, 5.54; Sn, 71.99. Calc. for $C_6H_{18}Sn$: C, 22.00; H, 5.54; Sn, 72.47%).

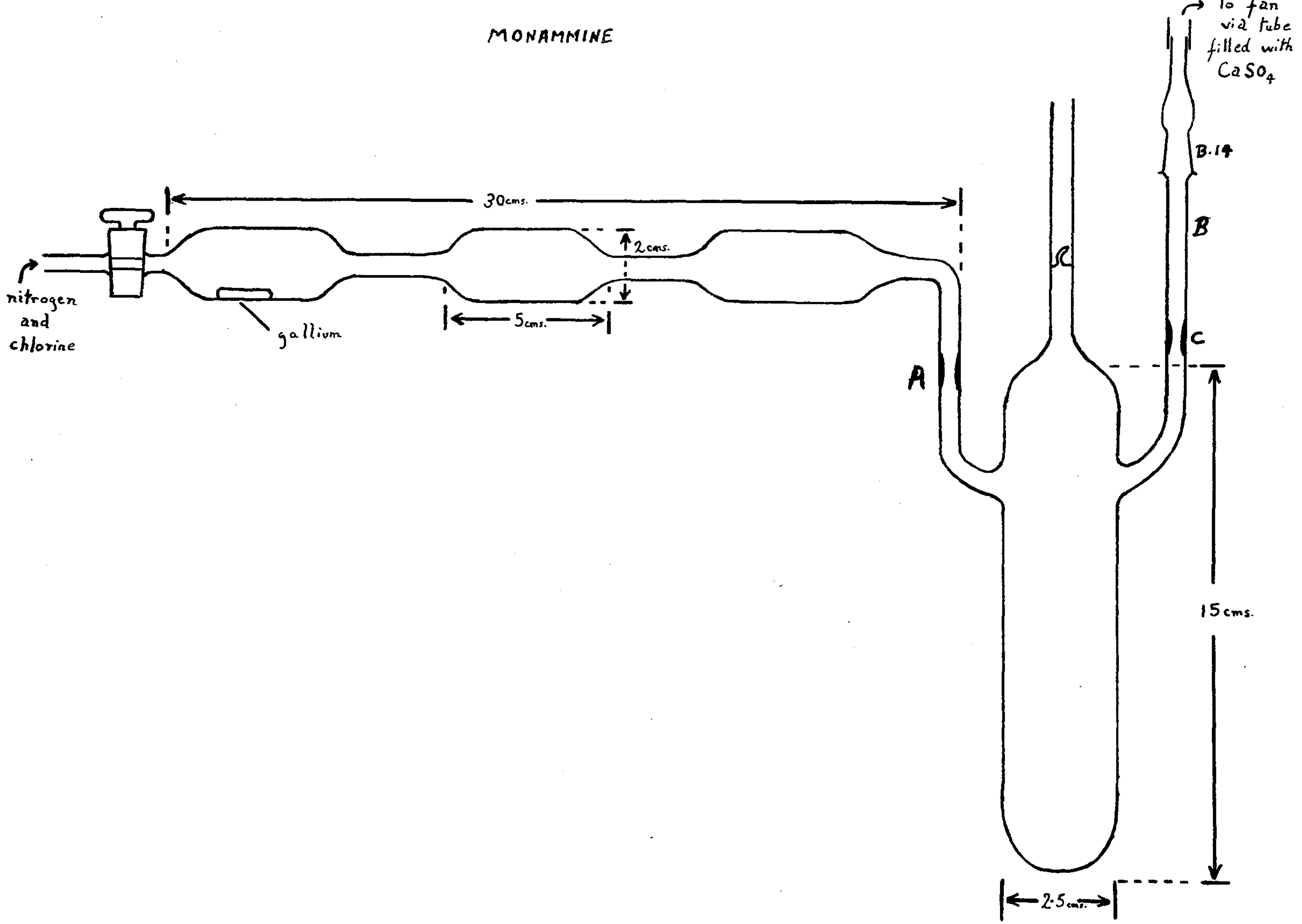
The formation of hexamethylditin was thus confirmed in 55.2% yield (liq. b.pt. 54.58°C./5.2 m.m.'s, 10 g.), based on the proportion (75/95) of trimethyltin lithium solution used.

The small amount of red solid filtered from the reaction mixture gave a white solid on exposure to air. An attempt to prepare a dichloride from this solid (suspected to be dimethyltin oxide) was unsuccessful.

(i) Reaction between Trimethyltin Sodium and Dimethylgallium Chloride in Liquid Ammonia

Although the previous experiment had indicated that the yellow-green solution produced by reaction between trimethyltin bromide and lithium contained trimethyltin lithium, it seemed that the original object of this work, *i.e.*, to establish metal to metal bonds, could only be achieved in liquid ammonia. The existance of trialkyltin alkali metal compounds in liquid ammonia is well established.[2,5-7,9] However, since nearly

PREPARATION OF DIMETHYLGALLIUM CHLORIDE MONAMMINE



all suitable organo-metallic halides are rapidly ammonolysed the choice was practically limited to gallium. Dimethylgallium chloride forms a stable ammine, which is not readily ammonolysed, and is freely soluble in liquid ammonia and ether (a diammine being insoluble in ether).

The preparation of dimethylgallium chloride ~~non~~ mano-ammine involved a three stage process:-

$$2Ga + 3Cl_2 = 2GaCl_3$$

$$2(CH_3)_3Ga + GaCl_3 = 3(CH_3)_2GaCl.$$

$$(CH_3)_2GaCl + 2NH_3 \longrightarrow (CH_3)_2Ga(NH_3)_2Cl \xrightarrow[60^{\circ}C.]{\text{in vacuo}} (CH_3)_2Ga(NH_3)Cl.$$

Gallium (3.5 g., 0.0503 mole) was introduced into the apparatus shown in the diagram, which was swept out by nitrogen dried by passage through concentrated sulphuric acid. A mixture of chlorine, dried by passage through concentrated sulphuric acid, and nitrogen was then passed through the apparatus. The gallium was heated gently, when formation of gallium trichloride occurred, most of which condensed in the second bulb. When the rate of reaction decreased more vigorous heating was employed to complete reaction. The bulk of chlorine was then swept out of the apparatus with nitrogen and residual traces removed by evacuating the apparatus for a few minutes. The gallium chloride was then distilled in a slow current of nitrogen into the third bulb leaving behind a deep brown residue. Finally the product was melted and allowed to run into the reaction vessel and the side-arm sealed at A. The reaction vessel was then attached to the vacuum system by side-arm B, evacuated, and trimethylgallium (11.54 g., 0.105 mole) was condensed into the reaction vessel, which was sealed at C. On warming up to room temperature reaction occurred with evolution of heat and the reaction vessel was cooled in ice-water. Finally reaction was completed by warming to *ca.* 45°C for 1½ hours. Unreacted trimethylgallium was removed from the dimethylgallium chloride by attaching the reaction vessel, *via* the centre lead, to the vacuum apparatus, breaking the seal by dropping a stainless steel ball-bearing onto it, evacuating, and condensing out at -30°C. Residual traces were removed by allowing the reaction vessel to warm to -15°C. for 15 minutes. The reaction vessel was then filled with nitrogen, removed from the vacuum system, and connected to a vessel containing liquid ammonia and sodium (to dry the ammonia) *via* one of the side-arms, the centre lead being used as an outlet for the system. Condensation of dry ammonia onto the dimethylgallium chloride yielded the diammine, which in turn, after removal of the bulk of excess liquid ammonia, yielded the monammine by pumping, *in vacuo*, at *ca.* 60°C. for 5 hours. Dimethylgallium chloride monammine (14.6 g., 0.096 mole) in 61.8% yield was obtained.

$$(CH_3)_3SnNa + (CH_3)_2Ga(NH_3)Cl = (CH_3)_3Sn\text{-}Ga(CH_3)_2 + NaCl + NH_3.$$

Trimethyltin sodium was prepared in dry liquid ammonia (*ca*. 70 c.c.'s) from trimethyltin bromide (17.6 g., 0.072 mole) and sodium (3.3 g., 0.194 mole) kept cool by an acetone/carbon dioxide bath and under nitrogen. An equivalent amount of dimethylgallium chloride monammine (11.1 g., 0.073 mole) in ether (50 c.c.'s) was then added to the stirred solution of trimethyltin sodium. A white precipitate formed immediately. Ammonia was allowed to boil off overnight and then the residual mixture was filtered under nitrogen to remove solid (NaCl, NaBr), yielding a pale yellow solution. Concentration of this solution by distillation under nitrogen left liquid (23 g.) which was slightly cloudy with a small amount of grey solid present.

A sample of the liquid (2 c.c.'s., 2.5 g.) was placed in a small distillation apparatus, which was kept at 50°C. while the pressure was slowly decreased. A small amount of liquid distilled at *ca*. 1.7 m.m.'s, further reduction of pressure having little effect on distillation. About 0.25 c.c. of liquid distilled and that remaining solidified on cooling. A tin analysis on the remaining solid gave the result of 17.5% tin. The corresponding values for the compounds $(CH_3)_3Sn-Ga(CH_3)_2$ and $(CH_3)_3Sn-\overset{-}{Ga}(\overset{+}{N}H_3)(CH_3)_2$ are 45.1% and 40.8% tin respectively. A test for nitrogen on a sample of the solid (after breakdown by sodium) was positive and halogens were absent.

The liquid remaining (20.5 g.) was then pumped down to *ca.* 0.1 m.m. to remove residual ether leaving a viscous liquid (13.7 g.). A very small amount of solid was collected with the ether in a liquid nitrogen trap (probably hexamethylditin, m.pt. 23°C.). A sample of the viscous liquid (7.4 g.) was placed in a double Schlenk tube (page 21), under nitrogen. This sample solidified on local cooling with a piece of solid carbon dioxide as did the remaining viscous liquid. An equal mixture of *n*-pentane and methylene chloride was used to recrystallise the solid by freezing out from the saturated solution at room temperature using a solid carbon dioxide/acetone bath. The solid obtained, melted at 97-100°C. ($\left[(CH_3)_2\overset{-}{Ga}\overset{+}{N}H_2\right]_2$, m.pt. 97°C.). A sample of this solid was sublimed at 100°C. and 14.5 m.m.'s (calculated vapour pressure[37] of $\left[(CH_3)_2\overset{-}{Ga}\overset{+}{N}H_2\right]_2$ at 100°C. is 14.46 m.m.'s), however, the melting point of the product decreased to 74-88°C. Both the qualitative tin test and analysis for tin showed that the element was absent.

The solvent remaining in the Schlenk tube was removed by pumping, *in vacuo*. Solid remaining was extracted with cold *cyclo*-hexane, in which the solid of m.pt. ~ 97°C. was not appreciably soluble. The residue after removal of *cyclo*hexane distilled at 46-49°C./3.2 m.m.'s. On redistillation at 3 m.m.'s a fraction (0.8 g.) b.pt. 43-44°C. was collected which crystallised on cooling. A test for tin after breakdown and carrying out a Group II separation was positive. There was no indication of gallium in Group III. The liquid which distilled at 43-44°C./3 m.m.'s was found to melt at 22-23°C, hexamethylditin:- m.pt. 23°C. (Found: C, 21.91; H, 5.59. Calc. for $C_6H_{18}Sn_2$: C, 22.00; H, 5.54%).

An analysis for gallium was carried out on a sample of the solid m.pt. ~ 97°C. by the method of Fetter and Swinehart[38] involving titration of a gallium solution with potassium ferrocyanide using a dead-stop end point technique. The result obtained gave the value of ca. 57% gallium (calculated value for $[(CH_3)_2\overset{-}{Ga}\overset{+}{N}H_2]_2$ is 60.2%) although this was not accurate as the deflections of the galvanometer used were small.

Another sample of the solid remaining after removal of ether amounting to 5.8 g. was used to ascertain the amounts of hexamethylditin and the solid, which was suspected to be dimethylgallium amide, and, in the latter case, to obtain a pure sample for analysis. Extraction of the solid with cyclohexane, under nitrogen, and then removal of solvent followed by distillation at 3 m.m.'s yielded liquid (1.7 g.) b.pt. 42-44°C. (this solidified on cooling). This solid represented, by proportion, 38.1% of the tin used in the reaction as hexamethylditin.

Solid remaining unextracted by cyclohexane and some solid left after the distillation at 3 m.m.'s above was sublimed at 100°C./14.5 m.m.'s yielding 2 g. solid. Grey material (tin) remained unsublimed. A sample of the sublimed solid melted at 96.5-97.5°C. ($[(CH_3)_2\overset{-}{Ga}\overset{+}{N}H_2]_2$, m.pt. 97°C.).

Another sample of solid recrystallised from cyclo-hexane was used for carbon/hydrogen analysis (Found: C, 19.97; H, 6.72. Calc. for $C_4H_{16}N_2Ga_2$: C, 20.74; H, 6.81%).

The rest of the sublimed solid, after recrystallisation, was used for a gallium estimation by a gravimetric method. A weighed sample of the solid in a silica crucible was decomposed by 50% nitric acid. When all solid had dissolved concentrated nitric acid was added. After the solution had stood for ca. 1 hour an attempt was made to remove excess nitric acid by gentle heating. A vigorous reaction occurred suddenly causing losses by spattering and the final value obtained ca. 54% gallium was very low. As no more of the solid remained, and there was no indication of the formation of the compound $(CH_3)_3Sn\text{-}Ga(CH_3)_2$ (or $(CH_3)_3Sn\text{-}\overset{-}{Ga}(\overset{+}{N}H_3)(CH_3)_2$), it was decided not to repeat the reaction. The sublimed solid (2 g.) assuming it to be dimethylgallium amide represented, by proportion, 63% of the gallium used in the reaction.

In the reaction between trimethyltin sodium and dimethylgallium chloride in liquid ammonia ca. 38% of the tin was recovered as hexamethylditin and 63% of the gallium as dimethylgallium amide.

(j) Analysis of Organo-Tin Compounds

Gravimetric Analysis of Tin (Method of Gilman and King[25]).

About 0.5 gm. of sample was placed in a previously weighed

60 c.c. silica crucible. The crucible was then partially immersed in an evaporating dish containing cold water. A solution of bromine in carbon tetrachloride (about 4% by weight) was added slowly with shaking until a permanent red colour persisted. It was found advantageous to add neat bromine when a few c.c.'s of the carbon tetrachloride solution had been used. Two c.c.'s of a mixture of concentrated nitric acid (one part) and concentrated sulphuric acid (six parts) was then added dropwise with shaking or agitating. A reaction generally set in with the first few drops of the acid mixture and a white precipitate formed and rose to the surface. After the first few drops of acid mixture had been added the mixture was left until reaction started. Then the rest of the acid mixture was added slowly. In like manner there was added 3-4 c.c.'s of a mixture of 1:1 concentrated nitric and sulphuric acids. There was then added 2 c.c.'s of concentrated nitric acid and 4-5 c.c.'s of fuming nitric acid.

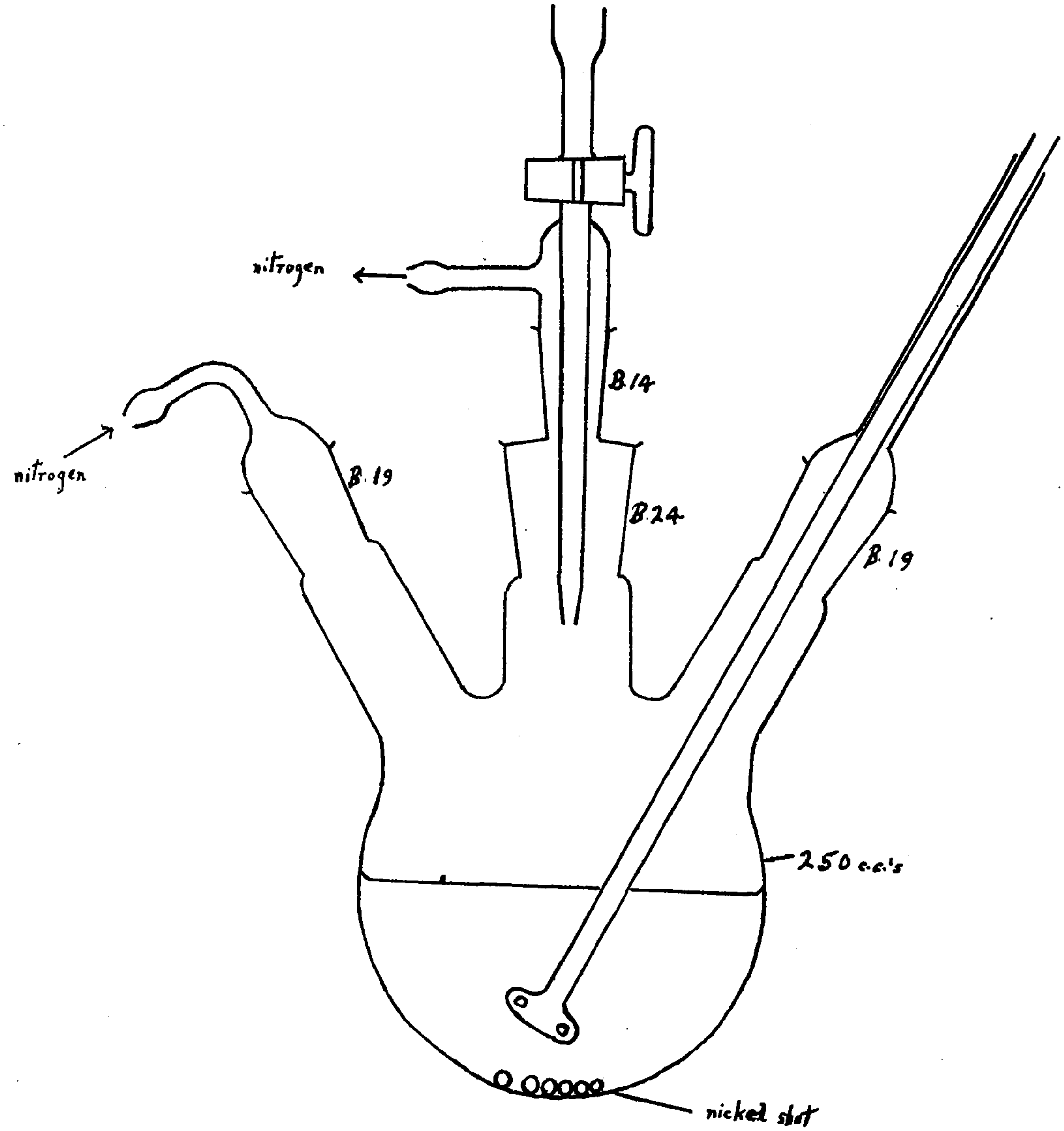
The crucible was then covered by a clock glass in a manner to permit ready escape of fumes, and allowed to stand on a water-bath for 30 minutes. The contents were then heated on an air-bath to expel residual oxides of nitrogen and the carbon tetrachloride until a clear solution remained. The watch glass was then removed and the crucible was heated until there was a slow evolution of sulphuric acid fumes. This was continued to remove all the acid. A grey residue was left. The crucible was then heated by means of a small direct flame until no more white fumes were evolved. Finally the crucible and contents were heated to constant weight using a Meker burner. The solid was weighed as stannic oxide (SnO_2).

Volumetric Estimation of Tin[26]

This method was found to be much more convenient than the method of Gilman and King[25], which has serious disadvantages. The gravimetric method implies removal of all involatile materials other than tin. The evaporation of the sulphuric acid was slow and made difficult by the fact that spattering occurred readily. In the volumetric method described the removal of many elements was unnecessary and the break-down procedure was carried out in a kjeldahl flask, thus preventing loss by spattering.

A sample of the tin compound (0.5-1 gm.) was placed in a kjeldahl flask (100 c.c.'s capacity). The break-down procedure was essentially that of Gilman and King[25] as described previously, except that a greater amount of concentrated sulphuric acid was used. The mixture was heated by means of a micro burner until the bulk of nitrogen fumes were expelled. As the presence of nitrates interfered with the subsequent titration residual nitrates were removed by adding solid ammonium oxalate to the mixture and heating until a clear solution resulted and no more brown fumes were visible on continued heating. If, after expelling

VOLUMETRIC ESTIMATION OF TIN



the bulk of nitrogen fumes by heating, the solution was not clear more fuming nitric acid was added and the heating was continued to give a clear solution. The final clear solution was diluted by the addition of a few c.c.'s of water ($\sim$5 c.c.'s) and cooled under the tap. Too great a dilution is to be avoided as precipitation of hydrated stannic oxide occurs. Then concentrated hydrochloric acid was added, cooling, as necessary, under the tap. The solution was then transferred to a graduated flask (usually 100 c.c.'s) with concentrated hydrochloric acid and made up to the mark with this acid. It was generally found that by this method no precipitation of tin occurred. If, however, solid formed in the kjeldahl warming with concentrated hydrochloric acid was sufficient to dissolve it.

Aliquots of the solution (10 c.c.'s or 20 c.c.'s) were transferred, by pipette, to the apparatus shown in the diagram. A large volume of concentrated hydrochloric acid was then added (80-100 c.c.'s). A short air condenser was fitted in place of the burette. Reduction by nickel was carried out with vigorous stirring under nitrogen to prevent atmospheric oxidation to the stannic state. The nickel used was in the form of Mond pellets (about 3 m.m.'s diameter). It was found that vigorous boiling (40-50 minutes) was necessary to complete reduction of tin to the stannous state. After reduction was complete the solution was cooled with cold water to room temperature, when evolution of hydrogen ceased completely. The air-condenser was removed, in a vigorous stream of nitrogen to prevent ingress of air, a c.c. of starch solution was added and then the burette was fitted to the apparatus. The solution was then titrated with iodine (about 0.1N) to a permanent blue colour. The solution was stirred continuously during titration. As the presence of dissolved oxygen in the iodine affects the end point the iodine was standardised against a standard tin solution before each estimation. The standard tin solution was made by dissolving a known weight of tin (analar purity) in concentrated hydrochloric acid and making up to a known volume (about 5N to hydrochloric acid). Aliquots (20 c.c.'s) of this solution were reduced in the way described and titrated with the iodine solution.

This method was also adaptable to estimation of air-sensitive tin compounds. The sample was weighed in a stoppered flask under nitrogen. An air-condenser, lubricated with concentrated sulphuric acid at the standard joint, was fitted to the flask. After weighing breakdown in air was carried out as described using a kjeldahl flask.

Characterisation of Di- and Tri- Alkyltin Compounds

The halides and dihalides of the lower tri- and dialkyltin compounds cannot generally be used for characterisation of the alkyltin radical since they are usually low melting solids or liquids. Corresponding fluorides being ionic are high melting solids which usually sublime below their melting points and are therefore also unsuitable as derivatives for characterisation.

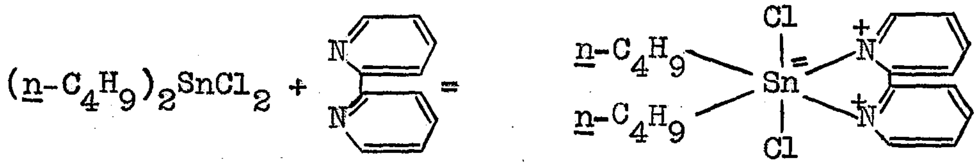
The chemistry of some of the lower trialkyltin acetates, which has been reviewed recently,[19] showed that they were suitable derivatives for the characterisation of trialkyltin radicals. The oxide or hydroxide was usually heated with glacial acetic acid to about 120-130°C. for 30 minutes to remove water formed in the reaction:-

$$(R_3Sn)_2O \; + \; 2CH_3COOH \; = \; 2R_3SnOCOCH_3 \; + \; H_2O.$$

Trialkyltin halides were converted to the oxide or hydroxide by shaking on ethereal solution with sodium hydroxide solution. Evaporation of the ether afforded the oxide or hydroxide. The acetate was recrystallised from light petroleum. In this research the tri-<u>n</u>-butyltin radical was characterised as its acetate, m.pt. 84°C.

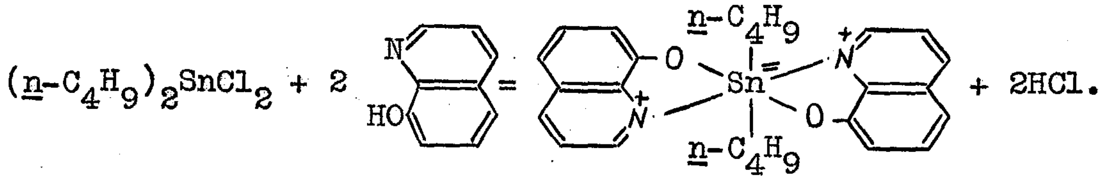
The characterisation of dialkyltin compounds, with particular reference to the di-<u>n</u>-butyltin radical, presented some difficulties as suitable derivatives did not appear to have been reported. However, alkyltin complexes with ammonia and pyridine had been reported[27,28]. This fact was made use of for the preparation of two new compounds for the identification of the di-<u>n</u>-butyltin radical.

Dipyridyl Complex



The complex was prepared by adding dipyridyl (1 mole) in alcohol to di-n-butyltin dichloride (1 mole) also in alcohol. A white precipitate formed immediately. This solid could be recrystallised in colourless needles from either alcohol or a mixture of petrol ether (80-100°) and benzene, m.pt. 179.5-180°C. (Found: C, 46.89; H, 5.89. $C_{18}H_{26}N_2Cl_2Sn$ requires C, 47.00; H, 5.70%).

Oxine Derivative



The oxine derivative was prepared by adding oxine (2 moles) in alcohol to di-n-butyltin dichloride (1 mole) in alcohol and adding sodium acetate in aqueous alcohol. A small amount of aqueous ammonia was added to decrease the acidity further. A yellow solid was precipitated. The solid was recrystallised from either alcohol or petrol ether (80-100°) as yellow plates, m.pt. 154.5-155.5°C. (Found: C, 59.53; H, 5.84. $C_{26}H_{30}N_2O_2Sn$ requires C, 59.92, 5.80%).

4. Discussion of Results

(a) Reactions in Tetrahydrofuran with Trimethyltin Bromide

The reaction between trimethyltin bromide and lithium in tetrahydrofuran was studied as a possibly convenient way of obtaining a tri-alkyltin alkali metal compound; the reaction which was expected to occur was,

$$(CH_3)_3SnBr + 2Li = (CH_3)_3SnLi + LiBr,$$

by analogy with the reaction which is known to occur in liquid ammonia. Lithium was used in preference to sodium since the lithium ion would be stabilised relative to the sodium ion by stronger solvation. The solvent used, tetrahydrofuran, has also a stronger solvating effect than diethyl ether on alkali metal ions. The pale yellow-green solution which was obtained after reaction between lithium and trimethyltin bromide was then used in reactions with organo-metallic halides. In the reactions carried out the pale yellow-green colour was discharged after reaction with the organo-metallic halides.

Silicon was used in the first reaction studied. As there were chemical similarities between tin and silicon (being members of the same group) and the fact that the compound triphenylsilicontriphenyltin had been reported[8] it was expected that formation of the compound trimethylsilicontrimethyltin would occur readily by the reaction:-

$$(CH_3)_3SnLi + (CH_3)_3SiCl = (CH_3)_3Si\text{-}Sn(CH_3)_3 + LiCl.$$

However there was no indication of such a compound although there was some indication of the formation of hexamethyldisilan in very small yield. No other tin compound was isolated from the reaction mixture.

As the first reaction had not yielded any expected product a reaction was then studied which was expected to yield a known compound. The pale yellow-green solution was allowed to react with triphenyltin bromide when the reaction,

$$(CH_3)_3SnLi + (C_6H_5)_3SnBr = (CH_3)_3Sn\text{-}Sn(C_6H_5)_3,$$

was expected to occur. The compound, trimethyltriphenyldi-tin, had been prepared from triphenyltin sodium and trimethyltin bromide in liquid ammonia.[9] Reaction again did not yield the expected product but hexaphenyldi-tin was isolated from the reaction mixture. This result pointed to a metal-halogen exchange reaction having occurred since this was the only conceivable mode of formation under the conditions of the reaction,

$$(CH_3)_3SnLi + (C_6H_5)_3SnBr \rightleftharpoons (CH_3)_3SnBr + (C_6H_5)_3SnLi$$

$$(C_6H_5)_3SnLi + (C_6H_5)_3SnBr = (C_6H_5)_3Sn\text{-}Sn(C_6H_5)_3 + LiBr.$$

An analogous reaction carried out in liquid ammonia between trimethyltin sodium and triphenyltin bromide also resulted in formation of hexaphenyldi-tin, hexamethyldi-tin and trimethyltriphenyldi-tin.[9] As mentioned above reaction between triphenyltin sodium and trimethyltin bromide yielded the expected product alone.

Although the previous reactions had not yielded any expected product, a reaction was carried out with an element from another group. The element used, arsenic, though not a metal, was a convenient element to start with before reactions with the more metallic members of the group antimony and bismuth, since a suitably reactive halogen derivative was readily available. A mixture resulted from the reaction between trimethyltin lithium and cacodyl chloride. This contained at least two components which could not be separated by distillation, one component being a low melting solid and soluble in the liquid mixture. This result again pointed to a metal-halogen exchange reaction having occurred, since the physical characteristics of the mixture were in accordance with the formation of cacodyl and hexamethyldi-tin:-

$$(CH_3)_3SnLi + (CH_3)_2AsCl \rightleftharpoons (CH_3)_3SnCl + (CH_3)_2AsLi$$

$$(CH_3)_3SnLi + (CH_3)_3SnCl = (CH_3)_3Sn\text{-}Sn(CH_3)_3 + LiCl.$$

$$(CH_3)_2AsLi + (CH_3)_2AsCl = (CH_3)_2As\text{-}As(CH_3)_2 + LiCl.$$

The boiling points of cacodyl (170°C.) and hexamethylditin (182°C.) at atmospheric pressure are close, thus making separation by distillation difficult, especially as a reduced pressure is necessary to prevent decomposition occurring.

Hexamethyldi-tin (m.pt. 23 °C.) is a low melting solid while cacodyl is a liquid (m.pt. $-4^{o}C$.); the mixed compound trimethyltindimethylarsenic, an unsymmetrical molecule, would be expected to melt lower than either of the above temperatures. Even if trimethyltindimethylarsenic were in the mixture its boiling point, which would be similar to hexamethyldi-tin and cacodyl, would make separation by distillation most unlikely.

Since the reactions using the yellowish-green solution produced by the reaction between trimethyltin bromide and lithium in tetrahydrofuran yielded neither expected nor desired products, it was decided that at such an early stage of the research further study of such reactions would be unprofitable. Therefore reactions that would confirm that the yellowish-green solution contained trimethyltin lithium were not carried out. From the reactions studied, however, it appeared that such was the case, since metal-halogen exchange reactions would seem to have been the most probable mode of formation of the reaction products, and these necessitated the existence of trimethyltin lithium.

(b) <u>Reactions with Sodium Methylsulphide and Sodium Methylselenide</u>

The reactions studied again involved the use of the trimethyltin group. The elements of Group VI being more electronegative than those of Group V, and consequently less metallic in character, it was expected that bonding of such an element to tin would occur readily. Some evidence of this was already known, compounds of the type R_3SnOR', had been reported being prepared by the reaction:-[29,30]

$$R_3SnX + R'ONa = R_3SnOR' + NaX.$$

These compounds are hydrolysed immediately by water to R_3SnOH and ROH. Compounds of the type $(RS)_4Sn$ had been prepared, and recently compounds similar to methyltriethyltin sulphide $((C_2H_5)_3SnSCH_3)$ have been described. The latter were prepared from the oxide ($[(C_2H_5)_3Sn]_2O$) and mercaptan.[31,32] Other compounds of the type $(R_3Sn)_2S$ and $(R_2SnS)_3$ have also been described.[33] There appeared to be no literature describing analogous compounds of selenium or tellurium.

The reaction between trimethyltin bromide and sodium methylsulphide, in methyl alcohol, yielded the expected product, methyltrimethyltin sulphide, in rather low yield (27%), which was probably due to losses incurred during working up rather than by side reactions.

Reaction between trimethyltin bromide and sodium methylselenide also yielded the expected product (approximately 70% yield). The product, methyltrimethyltin selenide, contained a tin-selenium bond, which does not appear to have been described in previous literature.

Thus, in the reactions carried out with the Group VI elements, sulphur and selenium, the expected reaction occurred.

Evidently there were no metal-halogen exchange reactions occurring in these cases. This may well have been due to the fact that the electronegative Group VI elements were in anionic form and thus most unlikely to undergo such exchange.

(c) Reactions of Cacodyl and Sodium in Liquid Ammonia

As the previous reactions, in which the trimethyltin radical was present in a cationic form, had been successful, the reaction between tin and arsenic was studied again, now using tin in cationic and arsenic in anionic form, the latter as dimethylarsenic sodium. Therefore, before the reaction between the tin and arsenic could be undertaken, evidence of the formation of the dimethylarsenic anion was required. Some evidence of the formation of a sodium or potassium derivative of diphenylarsenic had been reported by the addition of tetraphenyldiarsine to a sodium/potassium alloy in benzene.[34] An intensely yellow-brown colouration was produced. Addition of bromo-benzene to the solution afforded triphenylarsine, which was more conveniently handled and identified as triphenylmethylarsonium iodide, since this substance was easier to purify, in small amounts, than triphenylarsine. The similar reaction between cacodyl and sodium was studied in liquid ammonia, a much more convenient solvent for reactions of this type, _e.g._,

$$(CH_3)_2AsAs(CH_3)_2 + 2Na = 2(CH_3)_2AsNa.$$

The addition of an ethereal solution of cacodyl to sodium in liquid ammonia led to reaction in which the colour of the solution gradually changed from blue to a dark red-brown. The solvent was then replaced by ether and <u>n</u>-propyl iodide was added. In the presence of dimethyl-arsenic sodium the expected reaction was:-

$$(CH_3)_2AsNa \quad + \quad \underline{n}\text{-}C_3H_7I \quad = \quad (CH_3)_2\underline{n}\text{-}C_3H_7As.$$

Volatile material from this reaction was removed <u>in vacuo</u> and then allowed to react with methyl iodide to yield trimethyl-<u>n</u>-propylarsonium iodide:-

$$(CH_3)_2\underline{n}\text{-}C_3H_7As \quad = \quad CH_3I \quad = \quad (CH_3)_3\underline{n}\text{-}C_3H_7AsI.$$

The yield of the arsonium iodide however was low (23%). A similar reaction carried out using <u>n</u>-propyl bromide instead of <u>n</u>-propyl iodide yielded trimethyl <u>n</u>-propylarsonium iodide also in small yield (26%).

Although the above yields were low it was thought that they might be attributed to the following causes. There was the possibility of reaction between the <u>n</u>-propyl iodide (or bromide) and dimethylarsenic sodium yielding dimethyl-di-<u>n</u>-propylarsonium halide, which would not have been isolated under the conditions of reaction used. The arsonium halide, being a high-melting solid, would not be volatile, <u>in vacuo</u>, and would therefore not be removed from the reaction vessel. There was also the possibility of ammonolysis:-

$$(CH_3)_2As^- + \quad Na^+ \quad + \quad NH_3 \quad = \quad (CH_3)_2AsH \quad + \quad NaNH_2.$$

Any such arsine produced (dimethylarsine boils at 35°C.) would then probably have been lost during the removal of ammonia as considerable amounts of ether were also lost at the same time.

The fact that some of the expected arsonium iodide was obtained from the reactions suggested that dimethylarsenic sodium had been formed by the reaction between cacodyl and sodium in liquid ammonia. The reaction with trimethyltin bromide was therefore attempted.

In the preparation of dimethylarsenic sodium, the colour change indicating the end point when all the sodium had reacted was sharp; the solution suddently changed to a bright clear orange-red colour. The ethereal trimethyltin bromide solution was then added without removal of liquid ammonia as both it and the expected di-element compound would not be ammonolysed. A mixture resulted from this reaction, containing at least two components, which could not be separated by distillations under reduced pressure. The physical characteristics of the mixture were again consistant with formation of at least hexamethylditin and cacodyl as in the previous reaction between tin and arsenic, (page104).

(d) Reactions with tri-*n*-Butyltin Lithium

The compounds R_3SnLi are reported to result[1,8] when an alkyl- or aryl- lithium compound is added to a suspension of stannous chloride in ether at -10°C. The reaction proceeds via the dialkyltin stage, since when two moles of alkyl lithium have been added to one of stannous halide, the solution contains no alkyl lithium but dialkyltin. The dialkyltin then reacts with more alkyl lithium to yield the trialkyltin lithium:-

$$2RLi + SnX_2 = R_2Sn + 2LiX$$

$$R_2Sn + RLi = R_3SnLi.$$

n-Butyl tin compounds were used in preference to the ethyl compounds for two reasons. By the use of butyltin compounds with other compounds containing methyl groups it was hoped that the products of reaction would be of widely differing boiling points, thus facilitating ease of separation. There was some indication that dissociation of triethyltin lithium occurred, since a colour test with p-bromdimethylaniline became positive when only 2.5 moles of ethyl lithium had been added to one of stannous halide.[18] The colour test only becomes positive in the presence of an alkyl lithium (there is also evidence that triphenyllead lithium dissociates similarly in ether[35]). In the case of tri-n-butyltin lithium the colour test with p-bromdimethylaniline only becomes positive when three moles of n-butyl lithium have been added to one of stannous chloride.

When trimethylchlorsilane was added to a solution of tri-n-butyltin lithium there was no apparent colour change. No reaction appeared to have taken place in the first reaction (over 70% recovery of silicon) but the results of a second reaction indicated that tri-n-butyltin lithium dissociated in a similar manner to that of triphenyllead lithium and triethyltin lithium:-

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li.$$

The silicon was recovered as trimethyl-n-butylsilicon (54% yield) which must have resulted from the reaction:-

$$\underline{n}\text{-}C_4H_9Li + (CH_3)_3SiCl = (CH_3)_3\underline{n}\text{-}C_4H_9Si + LiCl.$$

This would be expected to occur in preference to the reaction,

$$(\underline{n}\text{-}C_4H_9)_3SnLi + (CH_3)_3SiCl = (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Si(CH_3)_3 + LiCl,$$

if dissociation had occurred, since n-butyl lithium (an extremely reactive compound) would be expected to react rapidly with trimethylchlorsilane, a reactive halide. This would drive dissociation of $(\underline{n}\text{-}C_4H_9)_3SnLi$ towards completion forming di-n-butyltin. There was, indeed, some evidence of this as a small amount of tetra-n-butyltin was obtained. Such a product would have resulted from decomposition of di-n-butyltin, especially on heating, as in this case, by the reaction:-

$$2(\underline{n}\text{-}C_4H_9)_2Sn = (\underline{n}\text{-}C_4H_9)_4Sn + Sn.$$

Gilman and Rosenberg[1] used tri-n-butyltin lithium to prepare tetra-n-butyltin and tri-n-butylphenyltin by the addition respectively of n-butyl iodide and iodobenzene. In the latter reaction it is interesting to note that an amount of tetra-n-butyltin equivalent to that of tri-n-butylphenyltin resulted.

The formation of tetra-n-butyltin in this reaction would in fact be expected if the dissociation,

$$(n\text{-}C_4H_9)_3SnLi \rightleftharpoons (n\text{-}C_4H_9)_2Sn + n\text{-}C_4H_9Li,$$

occurred, since the metal-halogen exchange reaction,

$$n\text{-}C_4H_9Li + C_6H_5I \rightleftharpoons n\text{-}C_4H_9I + C_6H_5Li,$$

would then most likely occur with formation of another organic halide (in this case n-butyl iodide). This type of reaction is well known to be both rapid and reversible even at low temperatures.[42-46] The position of equilibrium is dependent on the relative electronegativities of the organic radicals. In the case considered the amounts of iodobenzene and n-butyliodide, from an equimolar mixture of n-butyl-lithium and iodobenzene, have been shown to be almost equal by carbonation and estimation of the organo-lithiums as carboxylic acids.[23] Competitive reaction of the organic halides with the tri-n-butyltin lithium can then occur:-

$$(n\text{-}C_4H_9)_3SnLi + C_6H_5I = (n\text{-}C_4H_9)_3SnC_6H_5 + LiI$$

$$(n\text{-}C_4H_9)_3SnLi + n\text{-}C_4H_9I = (n\text{-}C_4H_9)_4Sn + LiI.$$

The reaction with methyl iodide was studied in order to obtain information about the nature of tri-n-butyltin lithium. Addition of methyl iodide to a solution of tri-n-butyltin lithium discharged the brown colour immediately, the solution becoming yellow. On warming to room temperature the solution became in turn milky white and then greyish, and finally on refluxing a brown colour. Only a small amount of methyltri-n-butyltin (14.4%) resulted from the expected reaction:-

$$(\underline{n}\text{-}C_4H_9)_3SnLi + CH_3I = CH_3(\underline{n}\text{-}C_4H_9)_3Sn + LiI.$$

Reactions on the red involatile liquid produced in this reaction, which was suspected to be di-n-butyltin, with methyliodide indicated that the tri-n-butyltin radical was also present in some form or other. Tri-n-butyltin acetate, which could not be purified, was obtained.

The amount of tin which could be accounted for in this reaction was less than half that used. This could not be explained. It was noticed however that ether removed from the reaction mixture by distillation became cloudy on exposure to air. This solid was found to contain tin. The formation of n-butyltin hydrides was suggested, these being the only products which would be volatile enough to be removed with ether. The hydrogen required for the formation of tin hydrides would probably come from the solvent with the formation of unsaturated material. In fact a small amount of unsaturated liquid (not containing tin) was obtained in this reaction. It thus seemed probable that some of the tin might have been lost in such a way.

The formation of both tri-n-butyl- and di-n-butyltin compounds in this reaction could arise from the following reactions:-

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li,$$

$$(\underline{n}\text{-}C_4H_9)_2Sn + (\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_3Sn\text{-}\overset{-}{S}n(\underline{n}\text{-}C_4H_9)_2Li^+,$$

$$2(\underline{n}\text{-}C_4H_9)_2Sn + (\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2\text{-}\overset{-}{S}n(\underline{n}\text{-}C_4H_9)_2Li^+, \ \underline{\text{etc}}.$$

n-Butyl-lithium, formed by dissociation of the trialkyltin lithium, could then react with the methyl iodide,

$$\underline{n}\text{-}C_4H_9Li + CH_3I = \underline{n}\text{-}C_5H_{10} + LiI,$$

yielding n-pentane, or undergo a metal-halogen exchange reaction:-

$$\underline{n}\text{-}C_4H_9Li + CH_3I \rightleftharpoons \underline{n}\text{-}C_4H_9I + CH_3Li.$$

Either the latter reaction did not occur to any appreciable extent, there being little indication of the formation of tetra-n-butyltin,

$$(\underline{n}\text{-}C_4H_9)_3SnLi + \underline{n}C_4H_9I = (\underline{n}\text{-}C_4H_9)_4Sn + LiI,$$

or the n-butyl iodide was removed rapidly by the reaction:-

$$\underline{n}\text{-}C_4H_9I + CH_3Li = \underline{n}\text{-}C_5H_{10} + LiI.$$

Thus the amount of methyltri-n-butyltin would be dependent on the relative rates of the reactions leading to formation of n-pentane, or tetra-n-butyltin and reactions of the type,

$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}\bar{S}n(\underline{n}\text{-}C_4H_9)_2Li^+ \; + \; CH_3I \; = \; (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2CH_3 \; + \; LiI,$$

and the reaction:-

$$(\underline{n}\text{-}C_4H_9)_3SnLi + CH_3I \; = \; CH_3(\underline{n}\text{-}C_4H_9)_3Sn + LiI.$$

Any $\underline{n}$-pentane (b.pt. 36°C.) formed in this reaction would have remained undetected in the ether (b.pt. 35°C.).

The reactions with carbon dioxide were expected to furnish more information about the nature of tri-$\underline{n}$-butyltin lithium especially with regard to the dissociation:-

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn \; + \; \underline{n}\text{-}C_4H_9Li.$$

When carbon dioxide was bubbled into a solution of tri-$\underline{n}$-butyltin lithium at approximately -10 to -20°C. the solution became more orange in colour. In the event of an equilibrium $\underline{n}$-valeric acid was expected to form:-

$$\underline{n}\text{-}C_4H_9Li + CO_2 \longrightarrow \underline{n}\text{-}C_4H_9CO_2Li \xrightarrow{HCl} \underline{n}\text{-}C_4H_9COOH.$$

However no valeric acid was formed in this reaction and there was no indication of the formation of oxalic acid. In other work carried out in this laboratory it had been shown that reaction between triphenyltin sodium and carbon dioxide in ether resulted in the formation of hexaphenylditin and sodium oxalate. Such a reaction was consistent with the formation of $[(C_6H_5)_3\bar{S}n\text{-}\bar{S}n(C_6H_5)_3]\ Na_2^+$, e.g.,

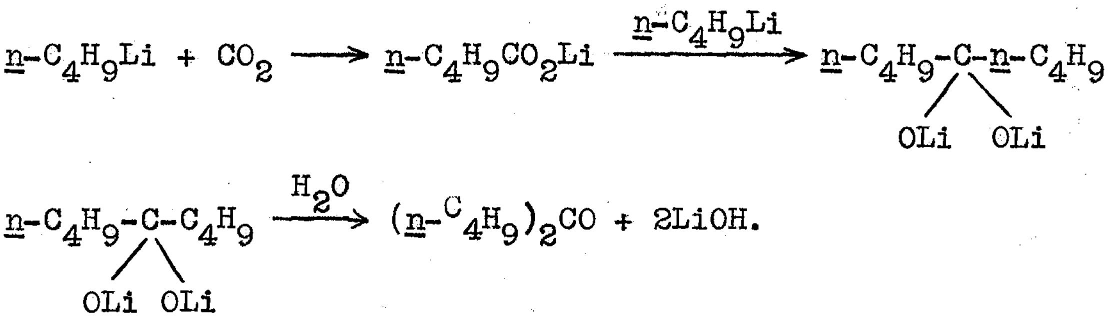
$$2(C_6H_5)_3SnNa \rightleftharpoons [(C_6H_5)_3\bar{S}n\text{-}\bar{S}n(C_6H_5)_3]\ Na_2^+,$$

$$[(C_6H_5)_3\bar{S}n\text{-}\bar{S}n(C_6H_5)_3]\ Na_2^+ + 2CO_2 = (C_6H_5)_3Sn\text{-}Sn(C_6H_5)_3 + 2CO_2^{-\bullet} + Na^+,$$

$$2CO_2^{-\bullet} = C_2O_4^{=}.$$

This does not apply in such a solvent as liquid ammonia, which has a high dielectric constant, where it would be present as $(C_6H_5)_3Sn^-Na^+$ as shown by the properties and reaction of such salts in liquid ammonia.

Di-n-butyl ketone was however produced in the reaction (37% yield) and identified as its semi-carbazone. The formation of ketones by carbonation of alkyl lithiums has been reported[20-22], especially where the alkyl lithium was in excess, as in this reaction:-



$$\underline{n}\text{-}C_4H_9Li + CO_2 \longrightarrow \underline{n}\text{-}C_4H_9CO_2Li \xrightarrow{\underline{n}\text{-}C_4H_9Li} \underline{n}\text{-}C_4H_9\text{-}\underset{OLi\quad OLi}{C}\text{-}\underline{n}\text{-}C_4H_9$$

$$\underline{n}\text{-}C_4H_9\text{-}\underset{OLi\quad OLi}{C}\text{-}C_4H_9 \xrightarrow{H_2O} (\underline{n}\text{-}C_4H_9)_2CO + 2LiOH.$$

Analysis of the non-volatile red liquid produced in the reaction showed that all the tin was present there. Solubility tests on this liquid showed that it was soluble in benzene and ether but insoluble in alcohol, which suggested a dialkyltin or alkyl tin-chain compounds. A reaction between a sample of this liquid and n-butyliodide in an attempt to prepare tri-n-butyltin iodide,

$$(\underline{n}\text{-}C_4H_9)_2Sn \;+\; \underline{n}\text{-}C_4H_9I \;=\; (\underline{n}\text{-}C_4H_9)_3SnI,$$

was unsuccessful, although an impure acetate obtained from the reaction mixture suggested that the tri-n-butyltin radical was present.

The presence of the tri-n-butyltin radical in the reaction mixture, however, could have arisen from establishment of the equilibrium already discussed (page 114):-

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn \;+\; \underline{n}\text{-}{}^{C}{}_4H_9Li,$$

$$(\underline{n}\text{-}C_4H_9)_2Sn + (\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_3Sn\text{-}\bar{S}n(\underline{n}\text{-}C_4H_9)_2Li^+,$$

$$2(\underline{n}\text{-}C_4H_9)_2Sn + (\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2 \\ \text{-}\bar{S}n(\underline{n}\text{-}C_4H_9)_2Li^+, \; \underline{etc}.$$

$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}\bar{S}n(\underline{n}\text{-}C_4H_9)_2Li^+ + \underline{n}\text{-}C_4H_9I \;=\; (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_3 \\ + LiI,$$

$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2\text{-}\bar{S}n\;(\underline{n}\text{-}C_4H_9)_2Li^+ + \underline{n}\text{-}C_4H_9I \\ = (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2\text{-}Sn(\underline{n}\text{-}C_4H_9)_3 + LiI, \; \underline{etc}.$$

$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2\text{-}Sn(\underline{n}\text{-}C_4H_9)_3 \xrightarrow[CH_3COOH]{NaOH} 2(\underline{n}\text{-}C_4H_9)_3SnOCOCH_3 \\ + (\underline{n}\text{-}C_4H_9)_2\;Sn(OCOCH_3)_2, \; \underline{etc}.$$

In a second experiment the ethereal mixture of tri-n-butyltin lithium was run onto a slurry of solid carbon dioxide and ether. By carbonation in this way it was hoped to keep formation of ketone to a minimum and obtain n-valeric acid.[20] From this reaction n-valeric acid (37.8%) and di-n-butyl ketone (22.6%) was obtained.

The red liquid from this reaction was dissolved in cyclo-hexane and oxidised by hydrogen peroxide. After treatment with concentrated hydrochloric acid and working up a liquid mixture was shown to contain di-n-butyltin dichloride and tri-n-butyltin chloride (as its acetate). It was not possible to separate the mixture completely. The chloride mixture obtained contained about half the tin used in the reaction.

The formation of tri-n-butyltin chloride and di-n-butyltin dichloride in this reaction, especially where the dissociation,

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li,$$

does not appear to have gone to completion (as shown by the yields of n-valeric acid and di-n-butylketone) can be explained in terms of the following reactions:-

$$(\underline{n}\text{-}C_4H_9)_2Sn + (\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_3Sn\text{-}\bar{S}n(\underline{n}\text{-}C_4H_9)_2Li^+,$$

$$2(\underline{n}\text{-}C_4H_9)_2Sn + (\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2\text{-}\bar{S}n(\underline{n}\text{-}C_4H_9)_2Li^+, \text{ etc.}$$

After oxidation and treatment with hydrochloric acid the tin compounds would then yield the mixture of mono- and di- chlorides:-

$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn^-(\underline{n}\text{-}C_4H_9)_2Li^+ \xrightarrow[HCl]{H_2O,H_2O_2} (\underline{n}\text{-}C_4H_9)_3SnCl + (\underline{n}\text{-}C_4H_9)_2SnCl_2,$$

$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2\text{-}Sn^-(\underline{n}\text{-}C_4H_9)_2Li^+ \xrightarrow[HCl]{H_2O,H_2O_2} (\underline{n}\text{-}C_4H_9)_3SnCl + 2\ (\underline{n}\text{-}C_4H_9)_2SnCl_2,\ \underline{etc}.$$

As the reactions already discussed in this section had shown that tri-n-butyltin lithium solutions in ether do not react entirely in the trialkyltin form, but also as a mixture of di-n-butyltin and n-butyl-lithium, the study of them was developed by bringing them into reaction with compounds, which were expected to give characteristic and well defined reactions with either the alkyl-lithium or the trialkyltin radical. The first reaction studied was that between tri-n-butyltin Lithium and β-phenylethylbromide, where the reaction,

$$(\underline{n}\text{-}C_4H_9)_3SnLi + C_6H_5CH_2CH_2Br = C_6H_5CH_2CH_2Sn(\underline{n}\text{-}C_4H_9)_3 + LiBr,$$

was expected to occur predominately, since the reaction,

$$\underline{n}\text{-}C_4H_9Li + C_6H_5CH_2CH_2Br = C_6H_5(CH_2)_5CH_3 + LiBr,$$

was expected to be relatively slower. It was therefore necessary to synthesize the unknown compound β-phenylethyl-tri-n-butyltin. The synthesis having proved successful, the reaction was carried out, but no single pure component was separated from the reaction mixture. The higher boiling liquids distilled from the mixture contained tin, and carbon and hydrogen values obtained from different fractions were reasonably consistent with mixtures of tetra-n-butyltin and β-phenylethyltri-n-butyltin, although the high percentage of carbon recorded in one fraction suggested that another component was present. Formation of such products is consistent with a metal-halogen exchange reaction,

$$\underline{n}\text{-}C_4H_9Li + C_6H_5CH_2CH_2Br \rightleftharpoons \underline{n}\text{-}C_4H_9Br + C_6H_5CH_2CH_2Li,$$

occurring, followed by reaction of the halides with the tri-alkyltin group:-

$$(\underline{n}\text{-}C_4H_9)SnLi + C_6H_5CH_2CH_2Br = C_6H_5CH_2CH_2Sn(\underline{n}\text{-}C_4H_9)_3 + LiBr,$$

$$(\underline{n}\text{-}C_4H_9)_3SnLi + \underline{n}\text{-}C_4H_9Br = (\underline{n}\text{-}C_4H_9)_4Sn + LiBr.$$

The exchange reaction is known to be rapid in contrast to the reactions which occur in a Wurtz-Fittig reaction, which would be expected to be relatively slow, e.g., in the general case,

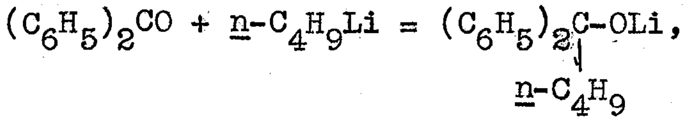
$$\begin{array}{llll}
RLi + R'X & \rightleftharpoons & RX + R'Li & \text{(rapid)} \\
RLi + R'X & = & R\text{-}R' + LiX & \text{(slow)} \\
RX + R'Li & = & R\text{-}R' + LiX & \text{(slow)} \\
RLi + Rx & = & R\text{-}R + LiX & \text{(slow)} \\
R'Li + R'X & = & R'\text{-}R' + LiX & \text{(slow)}
\end{array}$$

As the separation of the mixtures produced in the reaction was not feasible by distillation this reaction was not studied further. There was no indication of formation of large amounts of involatile red liquid in this reaction, indicative of organotin-chain compounds, so that the tin had evidently reacted predominantly in the trialkyltin form.

Addition of benzophenone to tri-n-butyltin lithium was expected to cause dissociation of the latter, e.g.,

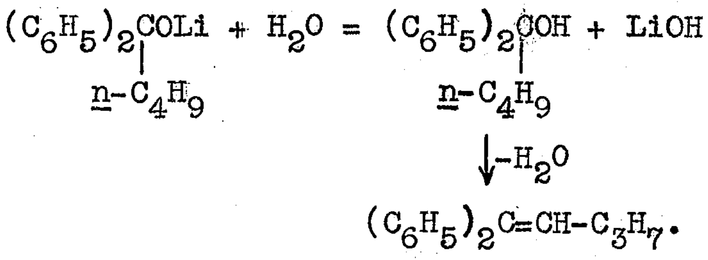
$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li,$$

since the reaction,



$$(C_6H_5)_2CO + \underline{n}\text{-}C_4H_9Li = (C_6H_5)_2\underset{\underset{\underline{n}\text{-}C_4H_9}{|}}{C}\text{-}OLi,$$

was expected to be relatively rapid. Analogous reactions carried out with the triphenylmetal lithium complexes of beryllium, magnesium, zinc and cadmium have been shown to yield appreciable amounts of triphenyl carbinol and the diphenylmetal. In the cases of beryllium and magnesium the diphenyl metal so formed can also react with benzophenone to yield more carbinol.[40] Subsequent hydrolysis of the reaction mixture in this case was then expected to yield the dehydration product of the carbinol:-



$$(C_6H_5)_2\underset{\underset{\underline{n}\text{-}C_4H_9}{|}}{C}OLi + H_2O = (C_6H_5)_2\underset{\underset{\underline{n}\text{-}C_4H_9}{|}}{C}OH + LiOH$$

$$\downarrow{-H_2O}$$

$$(C_6H_5)_2C{=}CH\text{-}C_3H_7.$$

The olive green colour produced on the addition of the benzophenone might have been due to an ion-radical electron transfer reaction of the type,

$$(\underline{n}\text{-}C_4H_9)_3SnLi + (C_6H_5)_2CO \rightleftharpoons (\underline{n}\text{-}C_4H_9)_3Sn\cdot + (C_6H_5)_2C^{\cdot}\text{-}O^{-}\}\ Li^{+},$$

red-orange blue

occurring, similar to the known reaction,[39]

$$(C_6H_5)C\}^{-}Na^{+} + (C_6H_5)CO \rightleftharpoons (C_6H_5)_3C^{\cdot} + (C_6H_5)_2C^{\cdot}\text{-}O^{-}\}\ Na^{+},$$

red colourless yellow blue

which also yields a green colour in ether. Such a colour, however, could have resulted from formation of $(C_6H_5)_2C^{\cdot}\text{-}O^{-}\}\ Li^{+}$ caused by the presence of small amounts of metallic lithium in the n-butyl lithium solution. On standing the green colour disappeared leaving an orange-red solution indicative of the formation of di-n-butyltin or organic tin-chain compounds (page 114). After oxidation of the reaction mixture, to convert the di-n-butyltin group to the insoluble oxide, the di-n-butyltin radical was characterised as both dichloride and the "oxine" derivative. Approximately 13% of the tin used in the reaction was recovered as the dichloride.

The ether soluble part of the reaction mixture on distillation yielded a high boiling fraction containing tin. The most probable tin compound boiling in this fraction (108°C/1 m.m.) was tetra-n-butyltin which has a similar boiling point (127°C/1.7 m.m., 109°C/0.5 m.m.). As however the carbon and hydrogen contents of the compound were respectively high and low for tetra-n-butyltin the presence of another compound of similar boiling point was suspected. The compound, $(C_6H_5)_2C{=}CH\text{-}C_3H_7$, an expected product of reaction, with a boiling point (125-6°C/1 m.m.) similar to that observed, and which would probably not be separated from tetra-n-butyltin by distillation, was therefore suggested. Further, the presence of such a compound as impurity in tetra-n-butyltin was in accordance with the high carbon and low hydrogen values found.

A higher boiling fraction (100-110°C, in vacuo) was found to consist of impure benzophenone, which was identified as its 2:4-dinitrophenylhydrazone, and represented approximately 23% recovery of the benzophenone used in the reaction. The red viscous involatile liquid produced in the reaction was of unknown constitution. It contained tin, which suggested di-n-butyltin or organic tin-chain compounds, but remained unchanged in colour after standing in air for an extended period and was soluble in alcohol (unlike di-n-butyltin). There was no indication that benzophenone was present.

As no well defined reaction had occurred between benzophenone and tri-n-butyltin lithium, although formation of the di-n-butyltin radical suggested that dissociation of tri-n-butyltin lithium occurred, further study of the reaction was discontinued.

Since the reaction between water and an alkyl-lithium is extremely rapid it was anticipated that reaction between water and tri-n-butyltin lithium would yield large amounts of n-butane, the dissociation of tri-n-butyltin being driven towards completion:-

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li\ ,$$

$$\underline{n}\text{-}C_4H_9Li + H_2O = \underline{n}\text{-}C_4H_{10} + LiOH.$$

However, only about 5% of the theoretical quantity of impure n-butane, in accordance with the above equations, was obtained. From the ether/tetrahydrofuran mixture there was obtained a red involatile liquid and a very small amount of liquid b.pt. 127°C/1.7 m.m.'s, which corresponded to that of tetra-n-butyltin (127°C/1.7 m.m.'s) and probably formed via decomposition of di-n-butyltin:-

$$2(\underline{n}\text{-}C_4H_9)_2Sn + = (\underline{n}\text{-}C_4H_9)_4Sn + Sn.$$

There was also evidence of the formation of tin since a small amount of grey solid, insoluble in either water or ether layers, was formed when reaction was carried out. The red involatile liquid was shown to contain the di-n-butyltin radical by oxidising a sample and converting the product, via the dichloride, to the "oxine" derivative. Similarly the tri-n-butyltin radical was shown to be present by the formation of the acetate.

Formation of tri-n-butyltin hydride,

$$(\underline{n}\text{-}C_4H_9)_3SnLi + H_2O = (\underline{n}\text{-}C_4H_9)_3SnH + LiOH,$$

evidently did not occur, since there was no indication of any other volatile material other than tetra-n-butyltin. Wittig, Meyer and Lange40, who carried out the analogous hydrolysis of triphenyltin lithium reported that hexaphenylditin was produced principally with hydrogen evolution, although some diphenyltin was also produced. The reaction was contrary to that which was observed to occur when the triphenylmetal lithium salts of beryllium, magnesium, zinc and cadmium reacted with water, since benzene and the metal hydroxides were usually produced. Wittig, Meyer and Lange[40] proposed that in hydrolysis of triphenyltin lithium, the lithium reacted as an alkali metal, liberating hydrogen with water and producing triphenyltin radicals, which dimerised to hexaphenylditin:-

$$2(C_6H_5)_3SnLi + H_2O = 2(C_6H_5)_3Sn^{\bullet} + 2LiOH + H_2$$

$$2(C_6H_5)_3Sn^{\bullet} = (C_6H_5)_3SnSn\ (C_6H_5)_3.$$

Therefore in the second reaction between tri-n-butyltin lithium and water provision was made for detection of hydrogen. The n-butane produced in this reaction was much purer and amounted to about 8% of the theoretical quantity in accordance with the equations mentioned previously. Hydrogen produced in the reaction was detected as water by passage through a heated copper oxide furnace, the water produced being absorbed by "anhydrone" and then weighed. The hydrogen collected in this way represented about 30% of that possible by the reactions:-

$$2(\underline{n}\text{-}C_4H_9)_3SnLi + 2H_2O = 2(\underline{n}\text{-}C_4H_9)_3Sn^{\bullet} + 2LiOH + H_2$$

$$2(\underline{n}\text{-}C_4H_9)_3Sn^{\bullet} = (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_3.$$

The formation of the red involatile liquid could arise from polymerisation of di-n̲-butyltin, formed by dissociation of tri-n̲-butyltin lithium, being initiated by the tri-n̲-butyltin radicals:-

$$(\underline{n}\text{-}C_4H_9)_3Sn^{\bullet} + (\underline{n}\text{-}C_4H_9)_2Sn \rightleftharpoons (\underline{n}\text{-}C_4H_9)_3Sn\text{-}\dot{S}n(\underline{n}\text{-}C_4H_9)_2,$$

$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}\dot{S}n(\underline{n}\text{-}C_4H_9)_2 + (\underline{n}\text{-}C_4H_9)_2Sn = (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2\text{-}$$
$$\dot{S}n(C_4H_9)_2,\ \underline{etc}.$$

The reactions being terminated by tri-n̲-butyltin radicals or dimerisation:-

$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}\dot{S}n(\underline{n}\text{-}C_4H_9)_2 + (\underline{n}\text{-}C_4H_9)_3Sn^{\bullet} = (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2\text{-}$$
$$Sn(\underline{n}\text{-}C_4H_9)_3,$$

$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2\text{-}\dot{S}n(\underline{n}\text{-}C_4H_9)_2 + (\underline{n}\text{-}C_4H_9)_3Sn^{\bullet} =$$
$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_2\text{-}\underset{\displaystyle Sn(\underline{n}\text{-}C_4H_9)_3}{\underset{|}{Sn}}(\underline{n}\text{-}C_4H_9)_2,\ \underline{etc}.$$

Formation of such products could also occur via̲ establishment of the equilibria mentioned previously,

$$(\underline{n}\text{-}C_4H_9)_3SnLi \rightleftharpoons (\underline{n}\text{-}C_4H_9)_2Sn + \underline{n}\text{-}C_4H_9Li,$$

$$(\underline{n}\text{-}C_4H_9)_3SnLi + (\underline{n}\text{-}C_4H_9)_2Sn \rightleftharpoons (\underline{n}\text{-}C_9H_9)_3Sn\text{-}\bar{S}n(\underline{n}\text{-}C_4H_9)_2Li^+$$

$$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}\bar{S}n(\underline{n}\text{-}C_4H_9)_2Li + (\underline{n}\text{-}C_4H_9)_2Sn \rightleftharpoons (\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn\text{-}$$
$$(\underline{n}\text{-}C_4H_9)_2\bar{S}n(\underline{n}\text{-}C_4H_9)_2Li^+,\ \underline{etc}.,$$

since, although the lithium of the tri-n̲-butyltin lithium would be expected to react very rapidly with water, in this case the lithium salts were in excess, i̲.e̲., addition of water to the tri-alkyltin lithium. Reaction of the compounds with water could then lead to radical formation with loss of hydrogen:-

$$2(\underline{n}\text{-}C_4H_9)_3Sn\text{-}\bar{S}n(\underline{n}\text{-}C_4H_9)_2Li^+ + 2H_2O = 2(\underline{n}\text{-}C_4H_9)_3Sn\text{-}\dot{S}n(\underline{n}\text{-}C_4H_9)_2$$
$$+ 2LiOH + H_2, \underline{\text{etc}}.$$

Since tri-n-butyltin lithium solutions had been shown to behave in a complex manner with a variety of reagents, and were not suitable for metal to metal bond syntheses, further investigations of such solutions were discontinued.

(e) Reaction between Trimethyltin Bromide and Lithium

Since the reactions in ether-like solvents had proved that trialkyltin alkali metal salts were not suitable reagents for metal to metal bond syntheses, a final reaction using the green solution produced when trimethyltin bromide and lithium reacted in tetrahydrofuran was carried out in order to produce further evidence that trimethyltin lithium was formed.

To a green solution produced by reaction between trimethyl bromide and lithium in tetrahydrofuran at -20°C. was added trimethyltin bromide, the green colour disappeared leaving an almost colourless solution. The reaction,

$$(CH_3)_3SnLi + (CH_3)_3SnBr = (CH_3)_3SnSn(CH_3)_3 + LiBr,$$

was expected to occur. During concentration of the reaction mixture by distillation decomposition appeared to occur, the solution turning a deep red-brown colour. Heating was therefore discontinued. As the presence of any trimethyltin bromide in the reaction mixture was objectionable, its boiling point being similar to that of hexamethylditin made removal necessary. The most suitable method involved treatmen with dilute alkali and acid in turn; such treatment had been shown to remove trimethyltin bromide completely from ether. However, since tetrahydrofuran was completely miscible with water replacement with ether was necessary. An attempt to remove more solvent under reduced pressure proved unsuccessful as there was indication that loss of hexamethylditin occurred. Therefore the reaction mixture was diluted with a large volume of ether and the trimethyltin bromide was removed as described. Losses of hexamethylditin may have occurred at this stage because of the increased solubility of water and ether in each other due to the presence of tetrahydrofuran, which is completely miscible in each. A small amount of red solid was observed at this stage in the reaction mixture. From the ether layer there was obtained on working up hexamethylditin in about 55% yield. Although this indicated that the green solution did contain trimethyltin lithium the possibility that the hexamethylditin, in such yield, could have originated by the reaction,

$$2(CH_3)_3SnBr + 2Li = (CH_3)_3SnSn(CH_3)_3 + 2LiBr,$$

could not be ruled out. However the fact that the reaction mixture produced by trimethyltin bromide and lithium was coloured, while the reaction above would yield a colourless solution, was further evidence in favour of the formation of trimethyltin lithium.

The small amount of red solid formed in the reaction was found to be air-sensitive, but an attempt to show that it was dimethyltin was unsuccessful.

Further study of tri-alkyltin alkali metal solutions in ether-like solvents was discontinued, since it was felt at this stage that only by the use of a liquid ammonia solvent that synthesis of metal to metal bonds might be achieved.

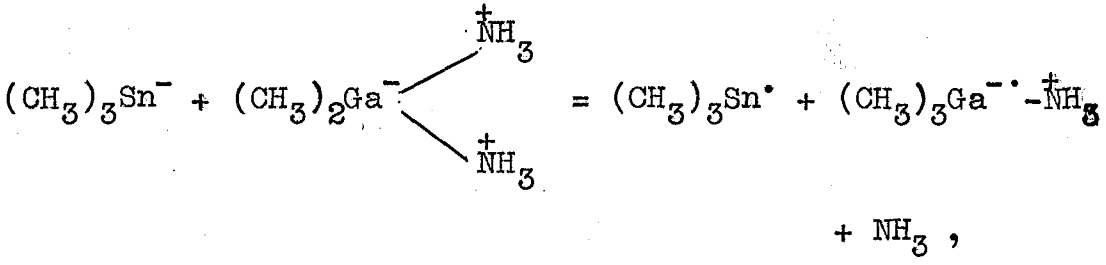
(f) Reaction between Trimethyltin Sodium and Dimethylgallium Chloride

Since the use of alkali metal derivatives of the trialkyltin radical as a synthetic reagent for coupling with reactive (especially organo-metallic) halides had been shown to be complicated by metal-halogen exchange reactions or by dissociation, it seemed that the original purpose of the work could only be achieved by the means of reactions in liquid ammonia. In this solvent no dissociation of the type discussed ($R_3SnLi \rightleftharpoons R_2Sn + RLi$) can occur, since alkali metal alkyls react instantly with ammonia and in fact solutions of trialkyltin alkali metal derivatives are stable in liquid ammonia.

Unfortunately nearly all of the halides with which alkali metal derivatives of the trialkyltin radical might usefully be brought into reaction with in order to establish metal to metal bonds are rapidly ammonolysed in liquid ammonia. The few exceptions to such ammonolysis are the organo-halides of some of the Group IIIB metals and mercury. Since compounds of the more noble metals, thallium and mercury, are readily reduced, the choice was even more limited and experiments with gallium were indicated. Dimethyl-gallium chloride forms a stable ammine, is not readily ammonolysed, and is freely soluble in liquid ammohia.

Addition of dimethylgallium chloride monoammine in ether to trimethyltin sodium in liquid ammonia resulted in instant precipitation of a white solid, and, after allowing ammonia to boil off, left a pale yellow supernatant solution. There was no indication of the formation of a compound containing a tin-gallium bond, and about 40% of the tin was recovered as hexamethylditin and about 60% of the gallium as dimethylgallium amide.

Formation of such products could have probably resulted by two mechanisms. The most probable reaction would involve an electron-transferrence reaction with formation of free radicals:-



$$(CH_3)_3Sn^- + (CH_3)_2Ga^-\left\langle\begin{array}{l}\overset{+}{N}H_3\\ \\ \overset{+}{N}H_3\end{array}\right. = (CH_3)_3Sn^\bullet + (CH_3)_3Ga^{-\bullet}\text{-}\overset{+}{N}H_3 + NH_3\ ,$$

$$2(CH_3)_3Sn^\bullet = (CH_3)_3SnSn(CH_3)_3\ ,$$

$$2(CH_3)_2Ga^{-\bullet}\text{-}\overset{+}{N}H_3 = \left\{(CH_3)_2\overset{-}{Ga}\overset{+}{N}H_2\right\}_2 + H_2\ .$$

An alternative reaction scheme involving metal-halogen exchange reactions,

$$(CH_3)_3SnNa + (CH_3)_2GaCl = (CH_3)_3SnCl + (CH_3)_2GaNa$$

$$(CH_3)_3SnNa + (CH_3)_3SnCl = (CH_3)_3SnSn(CH_3)_3 + NaCl$$

$$(CH_3)_2GaNa + (CH_3)_2GaCl = (CH_3)_2GaGa(CH_3)_2 + NaCl$$

$$(CH_3)_2GaGa(CH_3)_2 + 2NH_3 = 2(CH_3)_2Ga^{-\bullet}-\overset{+}{N}H_3$$

$$2(CH_3)_2Ga^{-\bullet}-\overset{+}{N}H_3 = \left\{(CH_3)_2\overset{-}{Ga}\overset{+}{N}H_2\right\}_2 + H_2,$$

seems more unlikely. There is evidence of the formation of an unstable substance $Na_2\left[(CH_3)_3GaGa(CH_3)_3\right]$ containing a gallium-gallium bond in liquid ammonia which decomposes above about -33°C.[41] On the other hand reduction of dimethylgallium chloride monoammine by sodium is known to occur in liquid ammonia,

$$(CH_3)_3\overset{-}{Ga}(Cl)\overset{+}{N}H_3 + Na = (CH_3)_3Ga^{-\bullet}-\overset{+}{N}H_3 + NaCl,$$

the orange colour of the solution being consistent with free radical formation.[41] Formation of $(CH_3)_2GaGa(CH_3)_2$ does not appear to occur, since such a compound would be expected to be colourless. The compound $(CH_3)_2Ga^{-\bullet}-\overset{+}{N}H_3$ decomposes at room temperature,

$$2(CH_3)_2Ga^{-\bullet}-\overset{+}{N}H_3 = \left\{(CH_3)_2\overset{-}{Ga}\overset{+}{N}H_2\right\}_2 + H_2,$$

with evolution of hydrogen.[41]

As the study of reactions of the trialkyltin alkali metal derivatives in ether solvents and liquid ammonia had not resulted in formation of metal to metal bonds between metals from different groups, further study of such reactions was felt to be unprofitable and the research topic was therefore concluded.

6. References

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Part II

Copperacetylide Complexes

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1. Introduction

The Present Investigation

The present investigation was concerned with the preparation of co-ordination compounds of organic copper- and silver- acetylides. Little work has been published on this subject, although recently Nast and Pfab[1] have shown that phenylcopperacetylide forms a weak co-ordination compound with ammonia. In other work carried out in these laboratories it has been shown that phenylcopper acetylide forms a much more stable triethylphosphine co-ordination compound.[2] Research was therefore directed towards the study of co-ordination compounds of copper and silver derivatives of mono-substituted acetylenes with amines, phosphines and arsines.

Co-ordination Chemistry of Copper^{I} and Silver^{I} Compounds

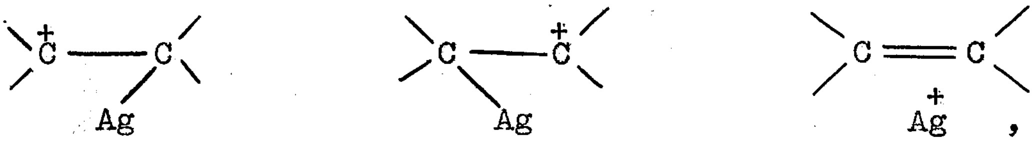
Copper and silver have a great tendency to form co-ordination compounds as might be expected from their high deforming power and position in the electrochemical series. The copper^{I} and silver^{I} halides (with the exception of the fluorides) are in some ways similar to the copper and silver acetylides in that they are essentially covalent in nature (silver chloride and bromide are ionic in the solid state but covalent in the vapour state[3]) and insoluble in aqueous and organi media. Thus, the co-ordination chemistry of copper^{I} and silver^{I} halides serves as a guide to the behaviour of the metal acetylides with various donor atoms.

Carbon Complexes

The alkyl and aryl compounds of copper and silver are ill-defined. Their stability decreases rapidly in the order aryl $>$ alkyl and copper $>$ silver $>$ gold.

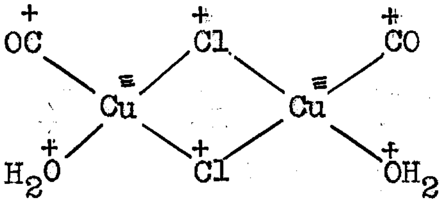
Thus cuprous iodide will dissolve in ethereal ethylmagnesium bromide at -18°C., yielding a green solution, which behaves as if it contains ethyl copper, but is extremely unstable and decomposes ~~rapidly~~ above -50°C.[4] Similarly Semeran and Riccoboni[5] prepared alkyl silver compounds from alcoholic silver nitrate and tetra-alkyl lead at -60° to -80°C. The products were precipitated from solution, but decomposed rapidly above -35°C. Phenyl copper was prepared from phenylmagnesium bromide, in ether, and cuprous iodide, a grey precipitate of the composition C_6H_5Cu being obtained.[4,6,7] This compound decomposed on heating to 80°C., or on standing, *in vacuo*, for two days, when a black mass resulted. Bolth *et al.*[8] have prepared various aryl coppers from copper and diazonium borofluorides at 80°C. These were only isolated as their pyridine complexes $ArCuPy_4$. Phenyl silver can be made from ethyltriphenyl lead or tin, $C_2H_5(C_6H_5)_3M$, (but not tetraphenyl- tin or -lead) and silver nitrate, a bright yellow, unstable powder of the composition $(C_6H_5Ag)_2.AgNO_3$ being obtained.[9] The aryl silver itself is precipitated as a dark solid when phenylmagnesium bromide reacts with silver chloride or bromide suspended in ether.[6,10] Phenyl silver decomposes violently when the ether evaporates, yielding diphenyl. Gardner[11] has made use of this decomposition to prepare various diaryls by the addition of the appropriate Grignard reagent to silver bromide suspended in ether, which was then refluxed; although the intermediate silver compounds were not isolated it is obvious that they must have been formed. Aurous alkyls and aryls are extremely unstable and have not been isolated from solution, but Kharasch and Bell[12] have shown that they are formed and obtained a solution of one of them.

It has long been known, however, that cuprous halides complex with ethylenes. Berthelot[13] showed that ethylene dissolves in a solution of cuprous chloride in hydrochloric acid and later Manchot and Brandt[14] showed that the compound formed approximated to the formula $CuCl.C_2H_4$. Tropsch and Mattox[15] and later Gilliland _et al._[16] showed that solid cuprous chloride will absorb olefins, mostly under pressure, the dissociation pressures of cuprous chloride complexes with ethylene, propylene and _iso_-butylene being 1 atmosphere respectively at -8.3°, -11.5 and -6.0°C. The complex formed between cuprous bromide and ethylene has a dissociation pressure of 17.5 atmospheres at 0°C. Lucas and his colleagues[17,18] have shown that silver also complexes with olefins. The structure of these compounds has been attributed to the formation of a resonance hybrid between the three structures,



this being supported by the Raman spectra of the complexes.[19] Acetylenes also co-ordinate in a similar way.[20] Approximate calculations have shown that the strain energy (ca. 4.5 K.cals.) is less than the resonance energy (ca. 10 K.cals.) of the silver-ethylene complex. No corresponding aurous compounds are known.

Cuprous halides form complexes with carbon monoxide, in the presence of water, ammonia, or bases such as aniline, piperidine and pyridine.[21-23] Dry cuprous chloride will only absorb carbon monoxide under high pressure, as compared with ethylene, which is absorbed readily, although no ethylene complex can be isolated. Since the empirical formula of the complex from water or concentrated hydrochloric acid solution is $CuCl.CO.H_2O$, and the solid product decomposes when treated with dehydrating agents such as concentrated sulphuric acid or alcohol, it is presumed that the complex is dimeric:



The central copper atoms have attained an effective atomic number of a rare gas (36), a phenomenon which appears to be common to most carbon monoxide complexes. This explains why the presence of water or a base is necessary in the carbon monoxide complex but not in the ethylene complex. No corresponding silver compounds have been isolated, but Manchot[24] has shown that silver sulphate, in fuming sulphuric acid, will absorb carbon monoxide at 0°C.

(ca. 0.86 mol. per Ag_2SO_4). The reaction is reversible since carbon monoxide is expelled on warming.

Manchot and Gall[25] have shown that gold forms a compound AuCl.CO from carbon monoxide and aurous chloride at 90°C; the same product results from carbon monoxide and auric chloride dissolved in tetrachloroethylene at 100-140°C.[12] This compound is, unlike the copper complex, decomposed by moisture yielding carbon monoxide and metallic gold.

Copper, silver and gold form a series of complex cyanide anions. The most stable cy ano-copper ion is $Cu(CN)_4^{\equiv}$, but the solid salts $M\,[Cu(CN)_2]$ and $M_2\,[Cu(CN)_3]$ are also known.[26,27] Kunschert[28] has shown, by e.m.f. measurements, that the anion $Cu(CN)_4^{\equiv}$ exists mainly in solution, but some $Cu(CN)_3^{=}$ is also present, especially in dilute solutions. This tendency of copper^{I} to form a 4-covalent complex is more pronounced with the cyanides than with any other cuprous complex. Silver also forms cyano-complexes, but in this case only the complexes $M\,[Ag(CN)_2]$ and $M_2\,[Ag(CN)_3]$ are stable. Brigando[27] has shown that the 4-co-ordinated silver complex is unstable. Gold only appears to form a dicovalent ion $Au(CN)_2^{-}$, which is more stable than the corresponding cuprous or argentous complexes.

Copper and silver, unlike gold, form complexes with *iso*-cyanides. Guillemand[29] prepared these compounds as early as 1908 by direct combination of the cyanide and *iso*-cyanide. Compounds of the type Cu(Ag)CN.RNC result (where R is an alkyl group) as colourless crystalline solids, which smell strongly of *iso*-cyanide. The copper complexes dissociate very readily and, on heating, the silver compounds decompose, a mixture of cyanide and *iso*-cyanide being liberated. The silver complexes are insoluble in water and many organic solvents, but soluble in alcohol. They are decomposed by strong acids and boiling aqueous alkalies.

Nitrogen Complexes

Both cuprous and argentous but not aurous compounds co-ordinate with cyanides. Rabaut[30] prepared the compounds from the cyanide and solid cuprous chloride. Similar compounds resulted when Morgan[31] added copper to a solution of cupric halide in a cyanide. These compounds are nearly all 1:1 complexes, *e.g.* $CuCl.CH_3CN$, except those of succinonitrile, which, having two cyanide groups, takes up two molecules of cuprous halide. The products are soluble in nitrile, but not in water, which slowly decomposes them. If the copper is oxidised to the cupric state with ferric ion, the cyanide is liberated.[30] Evidently only cuprous compounds can co-ordinate with cyanides. These halide complexes do not appear to be ionised, but a different type of complex results if a nitrate is used.

Thus, if copper is added to silver nitrate in acetonitrile, silver is precipitated and the copper replaces it. After removal of excess solvent a compound of the composition $[Cu(CH_3CN)_4]\ NO_3$ is left. This is stable while in acetonitrile solution, even in air, but if some nitrile is removed from the solid by passing an inert gas over it, decomposition occurs, even when air and moisture are excluded. A green solid and metallic copper are formed. This is a characteristic reaction of the cuprous ion, which is protected from the reaction by the weakly attached cyanide. Since decomposition occurs as soon as the cyanide content falls below four molecules, it appears that only the one complex is formed. Silver forms compounds with cyanides which are similar to those of copper, although few of them have been isolated. Silver nitrate is very soluble in acetonitrile, the solution being highly conducting, a complex salt of the type $[Ag(CH_3CN)_n]^+NO_3^-$ being indicated.[32] Silver nitrate forms complexes with bromo- and iodo-acetonitrile and even methylene iodide. These compounds are destroyed by water but otherwise reasonably stable, *e.g.* the compound $AgNO_3.CH_2I_2$ melts at $80^\circ C$.[33] Diels and Koll[34] have shown that reaction of th diacetate of hydrazomethane with copper sulphate leads to formation of a dark red solid, which with hydrochloric acid or sodium chloride yields the compound $CH_3-N{=}N-CH_3.2CuCl$. An iso-propyl compound containing water, $(CH_3)_2CH-N{=}N-CH(CH_3)_2.CuCl.2H_2O$, was also prepared, but this was very unstable. Silver and aurous complexes of this type appear to be unknown.

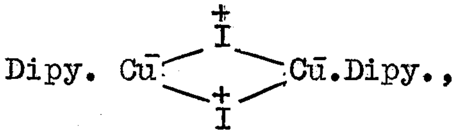
Both cuprous and argentous compounds form ammines containing up to three molecules of base. These compounds are generally soluble in water and conducting so that they are evidently of the type $[M(NH_3)_n]^+X^-$. From dissociation pressures Biltz[35] concludes that 4-co-ordinated cuprous ammines do not exist, although Abegg[36] has recorded a list of these salts which includes such compounds. Similarly Weinland[37] has described complexes containing four aniline or toluidine molecules, e.g. $[Ag(C_6H_5NH_2)_4]NO_3$, but gives no references or data.

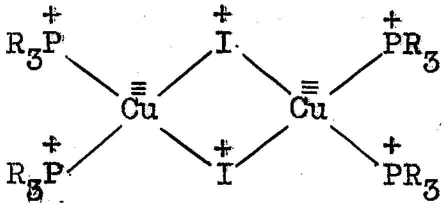
Aurous ammines of the type $[Au(NH_3)_n]^+Cl^-$ (n = 1 to 3) are also known, being prepared from aurous chloride and liquid ammonia.[38,39] These complexes decompose in water. Non-ionised ammines of the type $H_3\overset{+}{N}-\overset{-}{Au}-Cl$ were also prepared by Herrmann.[38] He obtained the complex $H_3\overset{+}{N}-\overset{-}{Au}-Cl$ by evaporating down an aqueous ammonia solution of aurous chloride. The product is colourless, insoluble in water, but dissolves in liquid ammonia probably with formation of the ionic compound $[Au(NH_3)_2]^+Cl^-$. It decomposes at 150-200°C. without melting. This di-covalent aurous complex is evidently similar to the much better known phosphine and arsine compounds, *e.g.* $(C_2H_5)_3\overset{+}{A}s\text{-}\overset{-}{A}u\text{-}Cl$.

Phosphorus and Arsenic Complexes

Monovalent copper, silver and gold form complexes with phosphines, arsines and with the strongest donor, phosphorus, the trichloride and trialkyl ester.

Addition of phosphine to an acid solution of cuprous halide in alcohol yields complexes of the type $CuCl.PH_3$, $CuBr.PH_3$ and $CuI.2PH_3$.[40] They are less stable than the ammines, which they resemble, phosphine being lost readily, *in vacuo*, and the compounds decompose readily to copper phosphide (Cu_3P). The order of stability is $Cl > Br > I$, as found for the ammines, but cuprous iodide, which should form the least stable complex, alone can take up two molecules of phosphine. Arbusov[41] prepared complexes of the silver halides by reaction with triethyl phosphite, *e.g.* $AgCl.P(OC_2H_5)_3$. Lindet[42] prepared the complex $AuCl.PCl_3$ by the addition of phosphorus trichloride to auric chloride in ether, which yields the compound on evaporation. This complex is insoluble in water, with which it reacts forming phosphorus acid. Alcohol converts the compound to the ester complex, $AuCl.P(OC_2H_5)_3$. The last compound also results from reduction of auric chloride with the alkyl phosphite in alcohol.

Mann *et al.*[43] and Burrows and colleagues[44] have described some particularly interesting complexes of cuprous and silver halides with trialkylphosphines and trialkylarsines, in which the copper appears to be 2-covalent. They were prepared by the action of the base on a concentrated solution of the cuprous or argentous halide in concentrated potassium halide solution. The products are obviously not ionic, since they are insoluble in water, but readily soluble in solvents such as benzene and acetone. Molecular weights carried out ebullioscopically in acetone and benzene and cryoscopically in benzene showed they were tetrameric, e.g. $\left[R_3\overset{+}{P}-\overset{-}{Cu}I\right]_4$. Wells[45] confirmed their structure by X-ray analysis of the triethylarsine-cuprous iodide complex. The analysis showed that the four cuprous atoms occupy the corners of a regular tetrahedron, with the four iodine atoms above the planes of the faces. The arsenic atoms lie on the line joining the centre of the tetrahedron to the copper atoms, their valencies being tetrahedrally arranged. Thus the copper atom is in fact 4-covalent, being attached to one arsenic atom and three iodine atoms, the valencies being tetrahedrally disposed. The analogous silver iodide complexes were also shown to possess the same structure by molecular weight and X-ray analyses. It is interesting to note that, although 3-co-ordinated cuprous complex amines are not generally stable $(NH_3)_3CuI$ looses ammonia readily,[46] amines of stronger donor power, such as dipyridyl (Dipy.), react with the complexes, $\left[R_3P.CuI\right]_4$, yielding compounds of the type Dipy.CuI.PR_3, which are monomeric. Such products by loss of alkyl phosphine yield polynuclear compounds, _e.g._  the co-ordination number remaining unchanged. Similar compounds formulated as CuI.2PR_3 described by Arbusow are undoubtedly similar:[43]



The complexes of the type $R_3\overset{+}{P}\text{-}\overset{-}{Au}\text{-}Cl$ were prepared by Levi-Malvano[47] from the alkyl phosphine or arsine and an aqueous alcoholic solution of chloroauric acid. These compounds differ from those of copper and silver, being monomeric and the gold thus 2-covalent. This is typical of gold^{I}, which rarely forms 4-covalent compounds, an example of the stability of the 2-covalent compounds which are peculiar to this part of the Periodic Table. This is marked in the two succeeding elements mercury and thallium (as in $[CH_3\text{-}\overset{+}{Tl}\text{-}CH_3]\ I^-$) and to a much less extent by bismuth.

<u>Oxygen Complexes</u>

Since copper and silver do not possess a great affinity for oxygen, the number of oxygen complexes is very small. In fact no cuprous open-chain complexes appear to be known, although certain chelate compounds containing oxygen are known (page 15). Silver is very like copper in this respect. The small affinity of silver for oxygen is shown by the fact that most silver salts are anhydrous, *i.e.,* in the solid state. In solution this does not hold true where weakly co-ordinated oxygen links may exist. Bathe[48] has in fact concluded, from the mobilities of complex silver cations containing ammonia, alkylamines and pyridine, and the mobility of the silver ion, that the latter is $[Ag(OH_2)_2]^+$.

Willstätter and Pummerer[49] have obtained evidence that pyrone forms complex salts with silver nitrate, although they did not obtain a pure product.

MacDougall and Allen[50] have shown that the solubility of argentous acetate is increased by addition of alkaline acetates, or even silver nitrate or perchlorate. They conclude that formation of a complex acetate, $M[Ag(OCOCH_3)_2]$, occurs, although no salt of this type appears to have been isolated.

No aurous complexes of gold, in which gold is bonded to oxygen, appear to be known.

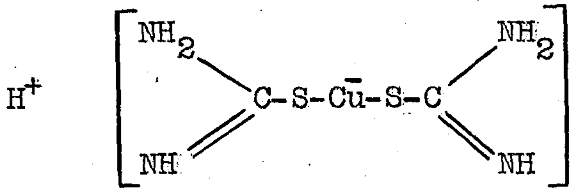
Sulphur Complexes

The affinity of copper, silver and gold for sulphur is much greater than that for oxygen, a considerable number of complexes being known. There are three main types of complex derived from thioethers, thioureas and polysulphides, such as $M(CuS_4)$.

Not many thioether complexes are known. The best known of this type, $(C_2H_5)_2\overset{+}{S}-\overset{-}{A}uCl$, was prepared by Mann, Wells and Purdie^{51} by the action of diethyl sulphide on auric chloride in hydrochloric acid. The product, a low melting, colourless, crystalline solid, is monomeric; ebullioscopic measurements in acetone showed that the association was 1.01 and cryoscopically in ethylene dibromide 1.09 and bromoform 1.10. A rather unstable dimorphic complex, $(C_6H_5CH_2)_2\overset{+}{S}-\overset{-}{A}uCl$, was prepared by Herrmann^{38} from excess of the sulphide and auric chloride. Analogous silver compounds are also known.^{52}

The complexes derived from compounds with the -C=S grouping are more numerous. Both copper and silver form complexes with thioacetamide of the type, $[M(SC(NH_2)CH_3)_4]\,X$.^{53} The analogous gold complex is characteristically 2-covalent, e.g. $[Au(SC(NH_2)CH_3)_2]\,X$.^{54}

The cuprous thiourea (Tu) and ethylene-thiourea (Etu.) complexes are numerous. Copper co-ordinates with up to three molecules of thiourea. Kohlschütter,^{55} who has examined these complexes in detail, has found that the copper is generally 3-covalent. An acid, probably,



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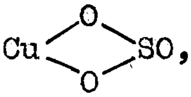
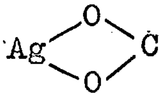
can be prepared and also a complex, $Cu(Tu.)_2Cl$. This latter is insoluble in water and therefore covalent as shown by conductivity and transport experiments. Some of the cuprous thiourea compounds are very complex, e.g. $[Cu_3(Tu)_7](NO_3)_3$, and it has been suggested that the amino group might take part in the formation of the complex, when it contains more than one copper atom.[56] Morgan and Burstall[56] have prepared a series of cuprous ethylene-thiourea complexes containing up to four molecules of the urea. The formulae of these complexes are rather peculiar, e.g. $[Cu(Etu.)_4]NO_3$; $[Cu(Etu.)_3]_2SO_4$; $[Cu(Etu.)_2]X$ (where $X = Cl$, Br or I) and $[Cu(Etu.)]_2O$. The complexes, with the exception of the latter, are strong electrolytes. In these compounds it is unlikely that the nitrogen in the ethylene-thiourea takes part in co-ordination, since it would involve the formation of a four-membered ring. Morgan and Burstall[56] have also prepared the analogous silver ethylene-thiourea complexes, which are very similar to those of copper, containing up to four molecules of the urea to one of silver. The latter authors also prepared gold complexes, which are of two types and remarkably stable, not being reduced to gold by formaldehyde. The complexes of the type $[Au(Etu.)_2]X$ (where $X = NO_3$, Cl , Br) are soluble in water and alcohol, but not ether or benzene, and are clearly ionic. Other complexes of the type Au(Etu.)I were also prepared, these being almost insoluble in water, covalent, and analogous to the amine, phosphorus and arsine complexes. Thus, the covalency of two is maintained in both types of complex.

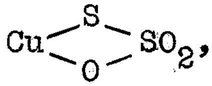
Only copper and gold form complex sulphides, each forming one distinct type of complex. Hofmann and Höchtlen[57] first established the formula of the complex copper sulphide, $NH_4\left[CuS_4\right]$, although the existence of the ammonium salt has long been known. Various alkali metal salts have been prepared and potassium and rubidium also form black salts of the type $M_2Cu_3S_{10}$.[58] Hofmann and Höchtlen[57,59] prepared the complex, $NH_4\left[AuS_3\right]$, from auric chloride and ammonium polysulphide. The product is yellow and almost insoluble in water.

Chelate Complexes

There are very few chelate complexes, and it is surprising that none of the metals will readily chelate with nitrogen compounds, although they all co-ordinate readily with ammonia. In fact the equilibrium, $2\overset{+}{Cu} \rightleftharpoons Cu^{++} + Cu$, lies well over to the right in the presence of ethylene-diamine, although ammonia stabilises the cuprous state. Most of the complexes are therefore those involving oxygen or sulphur or both, and, as mentionedpreviously, the affinity for sulphur is much stronger than that for oxygen.

Both copper and silver form complex sulphites, although the silver compounds are only known in solution. The copper complexes of the type $Na(CuSO_3)$ evidently contain the ring , the copper being 2-covalent.[60] Copper and silver also form carbonate-complexes. Donohue and Helmholz[61] have shown that the silver complexes contain the ring

, by X-ray analysis. Haase[62] as early as 1869 described an aurous complex sulphite of the composition $Na_3Au(SO_3)_2 \cdot 2H_2O$.

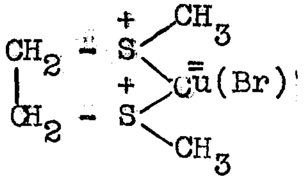
All three metals form complex thiosulphates. The cuprous thiosulphates are made by the action of alkaline thiosulphate on a cupric salt. A complex series of thiosulphate complexes can be made, but simple complexes of the type $KCu(S_2O_3)$ are known.[60] The stability of the complexes probably arises from formation of the ring , and the affinity of copper fo sulphur.

The analogous silver complexes were discovered in 1819 by Herschel[63] and have been used extensively in photography as a means of removing unreduced silver halide. Rosenheim and colleagues[60,64] and Meyer and Eggeling[65] have indicated that three types of complex are formed:

1) $M(AgS_2O_3)$, $M = Li.\frac{1}{2}H_2O$; Na, K, NH_4 anhydrous.
2) $M_3\left[Ag(S_2O_3)_2\right]$, $M = K.H_2O$
3) $M_5\left[Ag_3(S_2O_3)_4\right]$, $M = NH_4$, Na, K.

Of type one the lithium salt is readily soluble in water, but with the larger metal ions the solubility is markedly reduced. Gold forms 2-covalent salts of the type $M\left[Au(S_2O_3)\right]$, but these are less stable than the 4-covalent complexes $M_3\left[Au(S_2O_3)_2\right]$.[66,67] Here the chelation evidently stabilises the complex resulting in formation of a unusual covalency number of four for gold.

Copper and gold halides were shown to form sulphur-sulphur chelate complexes by Morgan and Ledbury.[68] Addition of dimethyldithiolethylene (thi.) to a cuprous salt yielded the pale blue complex $[Cu(thi.)]Br$, which is insoluble in water and organic solvents other than pyridine. The compounds evidently contain a five-membered ring and are formulated:-



Complex Halides

All the monovalent metals of Group 1B form complex halides. Copper forms a series of halide complexes of the type: $M[CuCl_2]$, $M_2[CuCl_3]$, $M_3[CuCl_4]$. Szabo and Szabo[69] have shown, by E.M.F. measurements, that in fairly strong potassium chloride solution (2 to 4 Normal) the chief complex ion is $[CuCl_3]^{=}$, the amount of $[CuCl_4]^{\equiv}$ present being negligible. Silver forms similar complexes, but there is doubt whether the type $K_3[AgI_4]$ exists.[70-72] Gold only forms complexes of the type $M[AuCl_2]$, the covalency of the metal being limited to 2. These complexes are unstable and aqueous solutions of them rapidly decompose yielding metallic gold.[73]

Elliot and Pauling[74] have shown that the highly complex $Cs.AuAuCl_6$ and $Cs_2AgAuCl_6$ contain linear $AgCl_2^-$ and $AuCl_2^-$ ions as well as planar ions $AuCl^-$. These salts are black, a common occurrence when one of the metal atoms is present in two different valency states.

Covalency Numbers of the Complexes

In these monovalent complexes the maximum covalency of copper, silver and gold is four. The chelate complexes are essentially more stable, this being due to the fact that if the chelate group has one of its bonds broken the ligand still remains attached by the other. The chelate complexes must necessarily form an even covalency, so that if the most favourable metal covalency is three then it is not surprising that either a 2 or 4-covalent complex is formed. Thus, even gold can form a 4-covalent chelate complex, although copper and silver also form them with sulphur compounds and the cyanides. Generally in the metal complexes the metal is 2 or 3-covalent, but there is a tendency for lower covalencies to be favoured as the group is descended and gold rarely exceeds the covalency of two.

2. Experimental

a) Preparation of Starting Materials

Preparation of 1:2 Dibromopropane

$CH_3CH = CH_2 + Br_2 = CH_3\text{-}CHBr\text{-}CH_2Br.$

1:2-dibromopropane (193.3 g., 100 c.c., 0.958 mole) was placed in a 1-litre 3-necked flask fitted with a gas inlet (below the liquid level), stirrer, dropping funnel and a gas outlet leading to a Drechsel bottle containing mercury arranged so that a pressure slightly above atmospheric was maintained in the apparatus. The flask was immersed in an ice/salt bath at -10°C. and a stream of propylene was passed into the 1:2-dibromopropane, which was stirred vigorously. Bromine (152 g. 0.953 mole) was then added from the dropping funnel at such a rate that the liquid was never deeply coloured by unreacted bromine. When the theoretical quantity of propylene (as measured by a gas flow-meter) had been added, the flask and contents were allowed to warm up to room temperature.

The reaction mixture was washed in turn with water and sodium carbonate solution, dried over magnesium sulphate, and distilled. A fraction b.pt. 139-141°C. amounting to 300.8 g. was obtained.

1:2 Dibromopropane (107.5 g. 0.532 mole) was obtained in 56% yield, after allowance was made for the initial amount used as solvent for the propylene. Further preparations led to formation of 1:2-dibromopropane in 66% and 67% yield respectively. A total of 1:2 dibromopropane (918.3 g., 4.55 moles) was obtained.

Preparation of Methylacetylene

(i). $CH_3CHBr-CH_2Br + 2KOH = CH_3C\equiv CH + 2KBr + 2H_2O$.

1:2-Dibromopropane (141.3 g., 73.3 c.c., 0.7 mole) was dropped slowly (over 2½ hours) onto a mixture of powdered potassium hydroxide (150 g., 2.68 moles) and n-butyl alcohol (300 c.c.) in a 1-litre flask heated to 160°C.[75] Volatile material, after passage in turn through a vertical air-condenser and water-condenser, was collected in two traps cooled by an acetone/solid carbon dioxide mixture (methylacetylene, b.pt. -23.1°C.). Liquid collected only in the first trap.

The methylacetylene so prepared was then converted to the mercury derivative for storage purposes.

$$2CH_3C\equiv CH + K_2HgI_4 + 2KOH = (CH_3C\equiv C)_2Hg + 4KI + 2H_2O.$$

The liquid in the trap was diluted with alcohol (20 c.c.) and added, while cold, to a stirred alkaline solution of potassium mercuri-iodide (132 g. 0.972 equiv. of mercuric chloride; 326 g., 1.22 equiv. of potassium iodide; 25 g., 0.62 equiv. of sodium hydroxide; 600 c.c. of water) cooled by an ice-bath. White solid was precipitated and, after stirring for 5 minutes after addition of the acetylene solution was completed, the solid was filtered and washed with 50% alcohol.[76] Methylmercuryacetylide (20 g., 0.072M) was obtained in 20.5% yield.

(ii). As the yield of methylacetylene from the first reaction was small, a preparation using liquid ammonia was carried out.[77]

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

$$CH_3CHBr-CH_2Br + 3NaNH_2 = CH_3C \equiv CNa + 2NaBr + 3NH_3.$$

$$CH_3C \equiv CNa + H_2O = CH_3C \equiv CH + NaOH.$$

Liquid ammonia (1,200 c.c.) was poured into a 2-litre 3-necked flask fitted with a dropping funnel, a stirrer containing a nitrogen inlet and a gas outlet. The flask was placed in a saucepan containing solid carbon dioxide. Air was excluded from the system by means of Drechsel wash-bottles containing heavy white oil. Sodium was catalytically decomposed to sodamide in the following manner.[78] Hydrated ferric nitrate (catalyst) 1 g. was added to the stirred liquid ammonia followed by sodium (2 g., 0.087 mole). On subsidence of the vigorous reaction a rapid stream of oxygen was passed into the liquid ammonia for a few seconds. This forms a small quantity of sodium peroxide, which activates the ferric nitrate. More sodium (76 g., 3.3 moles) was then added in <u>ca.</u> 15 g. quantities, time being allowed for all the sodium to react (loss of blue colour). The addition was completed in <u>ca.</u> 50 minutes. A grey solution (colloidal iron) resulted containing a fine suspension of reactive sodamide.

1:2-Dibromopropane (202 g., 1 mole) was then run into the liquid ammonia over 1 hour. Large amounts of liquid ammonia boiled off at this stage so that it was necessary to add more liquid ammonia, which was dried by the addition of a small piece of sodium. When addition of 1:2-dibromopropane was completed stirring was continued for an hour before the ammonia was allowed to boil off. Residual ammonia was removed by heating the reaction mixture on a water-bath, in a stream of nitrogen. The reaction vessel was then connected in turn to a gas wash-bottle containing 2N sulphuric acid (*ca.* 200 c.c.), a drying tower containing calcium chloride and two traps cooled by acetone/solid carbon dioxide mixtures. Methylacetylene was then liberated by decomposing the sodium salt with a saturated brine solution. The reaction was vigorous initially, but gradually moderated (addition of *ca.* 1000 c.c. of brine solution in 1 hour). Stirring was started as soon as the stirrer became free. Finally the reaction mixture was heated on a water-bath in a stream of nitrogen. It was found necessary to replenish the 2N sulphuric acid, the second portion of which was just alkaline at the end of the reaction. All the methylacetylene was collected in the first trap.

The methylacetylene was then converted to the mercury derivative as described in (i). Yellow solid was obtained in this case. After extraction with benzene a slightly pink solid (12.1 g., 0.043 mole) was obtained in 8.7% yield. The melting point of a sample after recrystallising twice from benzene was 200-201°C., with decomposition

($(CH_3C{\equiv}C)_2Hg$:- m.pt. 203-204°C.[76]).

(iii). The yields from the previous preparations were very low, but it was suspected that formation of the mercuryacetylide occurred in extremely low yield, since the preparation of methylacetylene in liquid ammonia is reported in 87% yield.[77] Another preparation was therefore carried out, in which the methylacetylene was stored as such in a vacuum apparatus.

Sodamide was prepared from sodium (47 g., 2.04 mole) in liquid ammonia (750 c.c.) as described previously. In this case, however, the reaction mixture was maintained at -50°C., by means of an acetone bath to which pieces of solid carbon dioxide were added, thus preventing large losses of liquid ammonia. 1:2-Dibromopropane (121 g., 0.60 mole) was added to the sodamide over 45 minutes, the liquid ammonia solution being maintained at -50°C. After stirring for another 30 minutes, ammonia was allowed to boil off. The methylacetylene was collected as described previously.

Since the product was to be converted to the cuprous and silver acetylides, the presence of acetylene (C_2H_2) was undesirable. The methylacetylene was therefore allowed to reflux up a short helices column, which was cooled at the top to -60°C., thus allowing any acetylene (b.pt. -88.5°C.) to escape (30 minutes). The remaining liquid was transferred to a vacuum apparatus, where it was stored as vapour. Methylacetylene (14.2 g., 0.364 mole) was obtained in 60% yield.

Preparation of Ethylacetylene[79]

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

$CH{\equiv}CH + NaNH_2 = CH{\equiv}CNa + NH_3.$

$(C_2H_5)_2SO_4 + CH{\equiv}CNa = C_2H_5C{\equiv}CH + C_2H_5NaSO_4.$

Sodamide was prepared from sodium (23 g. 1 mole) in liquid ammonia (600 c.c.) by the method described previously in a 2-litre 3-necked flask, fitted with a gas inlet below the level of the liquid (this was later replaced by a dropping funnel), a stirrer with a nitrogen inlet and a gas outlet, the solution being maintained at -50°C. Acetylene, purified by passage in turn through a trap cooled by an acetone/solid carbon dioxide mixture and a Drechsel bottle containing concentrated sulphuric acid, was bubbled rapidly into the stirred suspension of sodamide. The reaction mixture assumed a milky appearance initially but became darker after ca. 30 minutes and indicated that formation of sodium acetylide was complete.[80] Little loss of gas from the reaction vessel was observed up to this point. Complete formation of sodium acetylide was ensured by bubbling in acetylene for another 15 minutes. The outlet of the reaction vessel was then connected to an empty Drechsel bottle (acting as a safety trap) followed by an ammonia scrubber (a tower packed with glass helices down which water trickled, see Fig. 1), a conical flask containing 2N. sulphuric acid (1 litre) and phenolphthalein, a calcium chloride drying tower, two traps cooled to ca. -80°C and a Drechsel bottle containing heavy white oil, which excluded air from the system. Freshly distilled diethyl sulphate (170 g. 1.1 mole) was

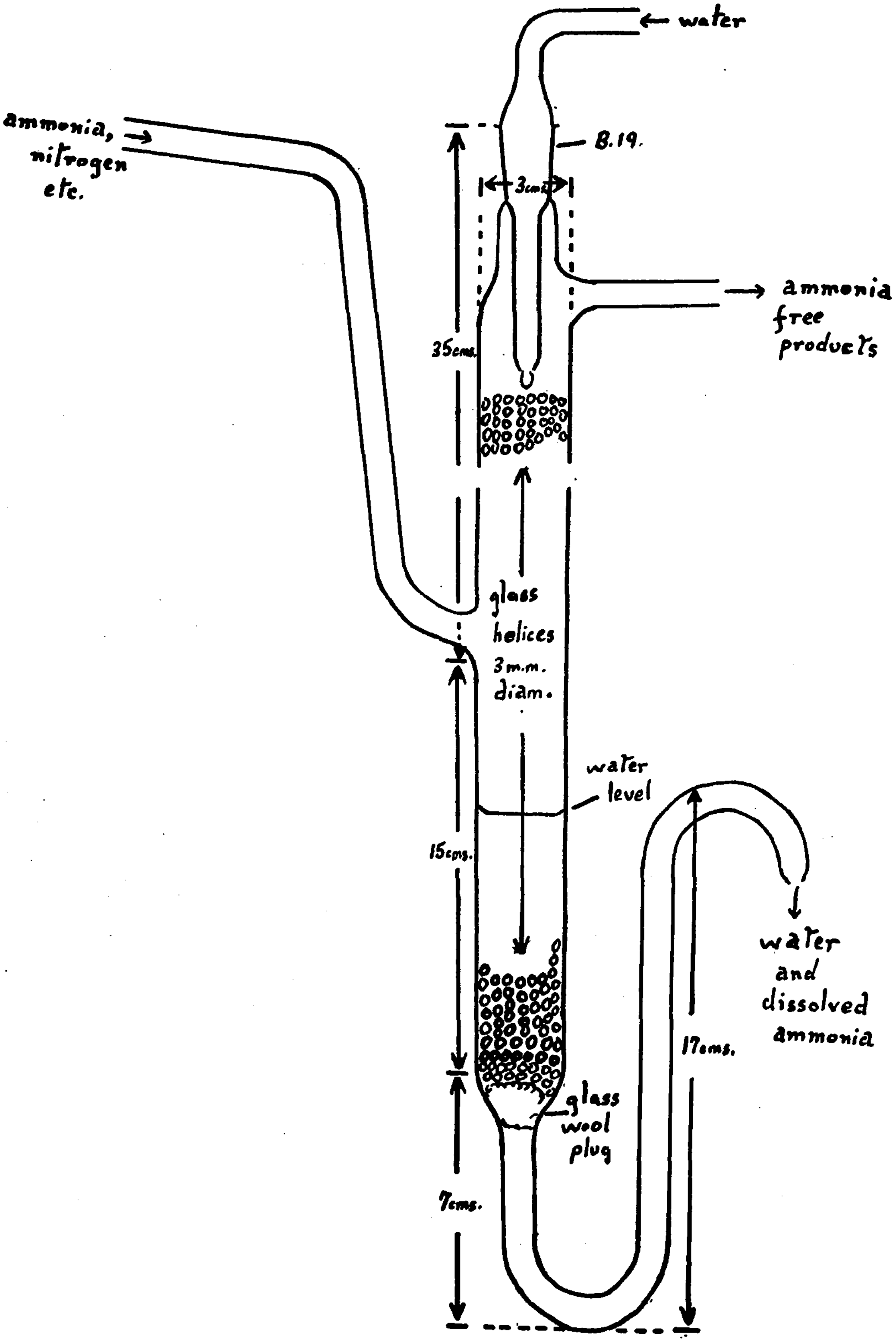

water
ammonia, nitrogen etc.
B.19.
3cms.
ammonia free products
35cms.
glass helices 3m.m. diam.
water level
15cms.
water and dissolved ammonia
17cms.
glass wool plug
7cms.

Figure 1.

then added over 1 hour. After stirring for another hour the ammonia was allowed to boil off. Water was then run into the reaction vessel, there being no evolution of heat. Complete removal of ethylacetylene (b.pt. 8.5°C.) was assured by heating the reaction vessel to *ca.* 75°C. for 15 minutes and passing a stream of nitrogen through it. Liquid was condensed only in the first trap cooled to -80°C. Any dissolved acetylene in the liquid was removed by refluxing the liquid up a short helices column cooled at the top to -50°C. (30 minutes). The residual material was then sealed in glass tubes after first cooling the ethylacetylene to *ca.* -80°C. Ethylacetylene (23.6 g., 0.437 mole) was obtained in 43.7% yield.

Preparation of *iso*-Propyl Sulphate[81]

$$2CH_3-CH=CH_2 + H_2SO_4 = (\underline{i}-C_3H_7)_2SO_4.$$

Concentrated sulphuric acid (294 g., 160 c.c., 3.0 moles) was placed in a 2-litre 3-necked flask fitted with a gas inlet below the surface of the acid, a stirrer and a gas outlet leading to a Drechsel bottle containing mercury, arranged so that a pressure slightly above atmospheric was maintained in the apparatus. Propylene was then passed into the acid, which was stirred vigorously, at a rate of about half a mole per hour, as measured by a gas flow-meter, the reaction vessel being maintained at *ca.* -3°C. by means of a salt/ice bath. After

6 moles of propylene had been passed into the acid (ca. 11½ hours), the contents of the flask were poured onto ice-water. Difficulty was experienced in separating the iso-propyl sulphate from the water because of emulsification. On washing the sulphate with cold water (3 times), the initial brown colour of the reaction liquid disappeared leaving a pale yellow, cloudy liquid. Finally the oily material was dried over a mixture of anhydrous potassium carbonate and magnesium sulphate. The cloudy appearance of the liquid disappeared, leaving a clear yellow liquid. After distillation under reduced pressure, iso-propyl sulphate (149.6 g., 0.82 mole) b.pt. 72°C./3 m.m. was obtained in 27.4% yield, as an almost colourless liquid. The distilling flask was not heated above 95°C., since it was found that decomposition was rapid above such a temperature. In a repeated run using sulphuric acid (184 g., 100 c.c., 1.88 moles) there was obtained iso-propyl sulphate (111.4 g., 0.61 mole) b.pt. 71°C./2.9 m.m. in 32.5% yield.

From a later preparation using sulphuric acid (368 g., 200 c.c., 3.76 moles) there was obtained iso-propyl sulphate (245 g., 1.35 mole) in 35.8% yield.

Attempted Preparation of iso-Propylacetylene.[81]

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$

$$CH\equiv CH + NaNH_2 = CH\equiv CNa + NH_3$$

$$(\underline{i}\text{-}C_3H_7)_2SO_4 + CH\equiv CNa = \underline{i}\text{-}C_3H_7C\equiv CH + \underline{i}\text{-}C_3H_7NaSO_4.$$

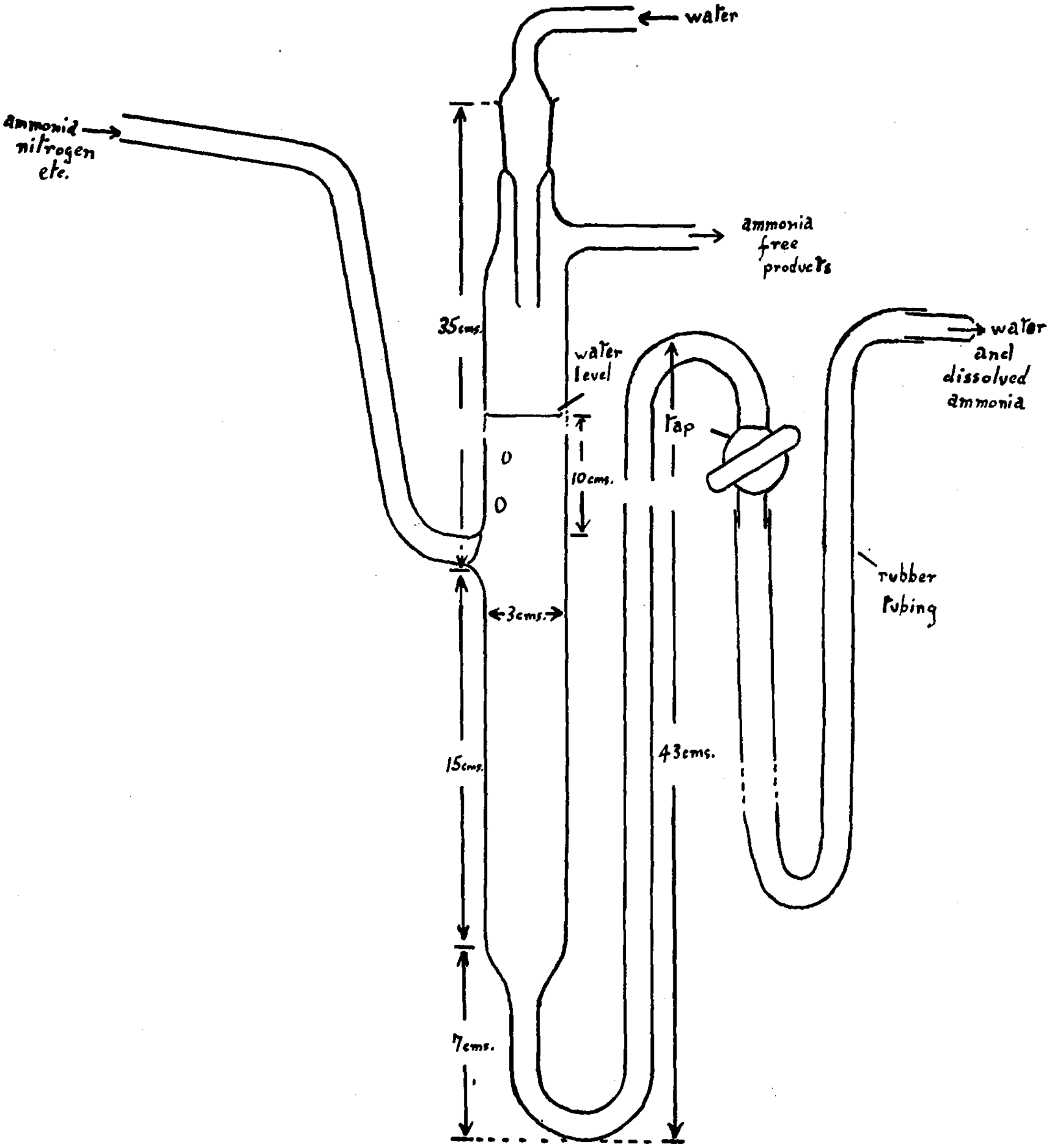
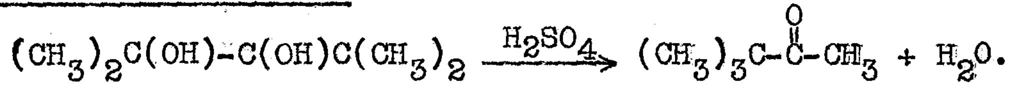

water
ammonia nitrogen etc.
ammonia free products
35cms.
water level
water and dissolved ammonia
tap
10cms.
3cms.
rubber tubing
15cms.
43cms.
7cms.

Figure 2.

Sodamide was prepared from sodium (21.8 g., 0.948 mole) in liquid ammonia (500 c.c.) at -50°C. in the usual way. Sodium acetylide was then prepared as described previously. The apparatus was then connected to a 1-litre conical flask acting as a safety trap, followed by an ammonia scrubber (Fig. 2), a conical flask containing 2N sulphuric acid (ca. 1 litre), a drying tower of calcium chloride, two traps cooled to ca. -80°C, and a Drechsel bottle containing heavy white oil (to exclude air from the system). The ammonia scrubber was not filled during the addition of freshly distilled iso-propyl sulphate (177 g. 0.974 mole), keeping the reaction vessel at -50°C. After the addition was completed (ca. 1¼ hour), the solution was stirred for another 15 minutes and then the ammonia was allowed to boil off, keeping a continuous head of water in the ammonia scrubber. This head of water (ca. 10 cms.) was controlled by means of the tap (A) and the height of the exit tube. When no more ammonia was evolved the reaction mixture was hydrolysed by addition of a saturated brine solution (1 litre), after which the reaction vessel and contents were heated on a water-bath (1 hour). Liquid was collected only in the first trap cooled to -80°C. This liquid was distilled through a short helices column and liquid b.pt. 31.5-32.5°C (13.0 g., a 20% yield of iso-propylacetylene) was obtained. From a second reaction starting from sodium (36 g., 1.57 moles) and using iso-propyl sulphate (240 g., 1.32 mole), there was obtained liquid b.pt. 32-33°C. (13.7 g., a 12.8% yield of iso-propylacetylene). The boiling point of iso-propyl ~~sulphate~~ acetylene is reported to be 29.3°C. All the liquid was stored in a vacuum apparatus.

Preparation of Pinacolone[82]

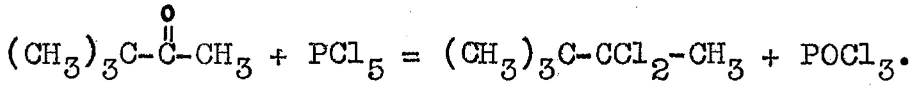


$$(CH_3)_2C(OH)-C(OH)C(CH_3)_2 \xrightarrow{H_2SO_4} (CH_3)_3C-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O.$$

Pinacol (130 g. 1.1 mole) was added to 6N sulphuric acid (750 c.c.) in a 2-litre flask arranged for distillation. The flask was heated by means of an oil-bath at ca. 140°C. A mixture of water and pinacolone was distilled and separated into two layers. After 15 minutes the bulk of pinacolone had distilled and heating was discontinued. The water and pinacolone layers were separated, the former being mixed with concentrated sulphuric acid (60 c.c.) and more pinacol (130 g. 1.1 mole) and returned to the 2-litre flask. Pinacolone was distilled as described before, the combined product being dried over magnesium sulphate. After fractionation by distillation through a short column, a main fraction b.pt. 101-107°C. was collected. More liquid b.pt. 101-108°C. was obtained on redistilling the initial and final fractions from the first distillation. Pinacolone (132.8 g., 1.33 mole) was obtained in 60% yield. From a second run there was obtained from pinacol (199.3 g., 1.52 mole), pinacolone (104.6 g., 1.05 mole) in 63% yield.

Pinacol (437 g., 3.7 mole) was converted in a later preparation to pinacolone (233.5 g., 2.34 mole) in 63% yield.

Preparation of 2:2-Dichloro-3:3-dimethylbutane[83,84]



$$(CH_3)_3C-\overset{O}{\overset{\|}{C}}-CH_3 + PCl_5 = (CH_3)_3C-CCl_2-CH_3 + POCl_3.$$

Pinacolone (132.8 g., 1.33 mole) was dropped slowly on to phosphorus pentachloride (280 g., 1.34 mole) in a 1-litre 3-necked flask fitted with a stirrer, dropping funnel and a water condenser with a drying tube containing calcium sulphate on the end. The flask and contents were cooled to 0^oC. bymmeans of an ice-bath. Stirring was only possible when sufficient pinacolone had been added to cause formation of a thick paste. The addition of pinacolone required ca. 3 hours. A deep red solution containing white solid was formed at this stage. After removal of the ice-bath the solution was stirred for another 5 hours, the solution becoming homogeneous and deep green. After standing overnight the solution was poured on to ice (800 g.) and stirred vigorously. The residual ice was allowed to melt and the mixture was filtered to collect the solid dichloride, which was air-dried. The aqueous phase was then neutralised with sodium bicarbonate and extracted with ether (2 x 200 c.c.). From the dried ether extract there was obtained, after distillation, a brown liquid, which deposited more of the solid dichloride on cooling. Crude 2:2-dichloro-3:3-dimethylbutane (110 g., 0.71 mole) was obtained in 53.5% yield. The brownish liquid also produced in the reaction consists mainly of 2-chloro-3:3-dimethylbutene-1

($(CH_3)_3C\text{-}CCl{=}CH_2$), which in this case amounted to 35 g. (0.295 mole), a 22.2% yield of crude material. From a second run using pinacolone (125.5 g., 1.26 mole) and phosphorus pentachloride (266 g., 1.275 mole), there was obtained 2:2-dichloro-3:3-dimethylbutane (98 g., 0.632 mole) in 50.2% yield and 2-chloro-3:3-dimethylbutene-1 (27.6 g., 0.273 mole) in 18.5% yield.

From a later reaction pinacolone (233.5 g., 2.33 mole) was converted to 2:2-dichloro-3:3-dimethylbutane (151.5 g., 0.98 mole) in 42% yield and 2-chloro-3:3 dimethylbutene-1 (79 g., 0.666 mole) in 28.6% yield.

Preparation of t-Butylacetylene

(i) $(CH_3)_3CCCl_2\text{-}CH_3 + 2KOH = (CH_3)_3C\text{-}C{\equiv}CH + 2KCl + 2H_2O$

$(CH_3)_3CCCl{=}CH_2 + KOH = (CH_3)_3C\text{-}C{\equiv}CH + KCl + H_2O.$

2:2-Dichloro-3:3-dimethylbutane (110 g., 0.71 mole) was mixed with powdered potassium hydroxide (395 g., 7.1 mole) in a 1-litre flask, fitted with a vertical reflux condenser, the top of which was connected to another condenser, to which an ice-cooled receiver was attached.[83,84] The flask was heated to 160°C., the flow of water in the vertical reflux condenser being adjusted so that the temperature at the top was about 40°C., thus allowing *t*-butylacetylene (b.pt. 35.5-36.5°C.) to escape and condense in the receiver, while retaining all other material in the flask.

The temperature of the reaction vessel was allowed to rise to 220°C. over a period of 6 hours. Only a small amount of liquid was collected in the receiver. Alcohol (45 c.c.) was therefore added to the cooled reaction products, which were reheated to 150°C. for 2 hours and 200°C for another 3 hours. All liquid collected in the receiver from this and the initial heating was combined and distilled through a column and liquid b.pt. 35.5-50°C. was collected. The contents of the reaction vessel were dissolved in water and extracted with ether, but little material remained after removal of ether and indicated that all the organic material had reacted or been destroyed.

The liquid left undistilled, after fractionation of *t*-butylacetylene, which consists of 2-chloro-3:3-dimethylbutene-1,[84] was added to more 2-chloro-3:3-dimethylbutene-1 (35 g., 0.295 mole prepared from the reaction between pinacol and phosphorus pentachloride, and mixed with powdered potassium hydroxide (300 g., 5.36 mole). Ethyleneglycol (150 c.c.) was added to provide a medium which would allow more intimate mixing of the chloride and potassium hydroxide. The mixture was heated in a 1-litre flask as described previously (7 hours), allowing the temperature to rise from 160-200°C. About 40 c.c. of liquid collected in the cooled receiver. This liquid was combined with the liquid from the initial heating and fractionated by distillation through a glass spiral column (ca. 50 cms. in height), the fraction b.pt. 36.0-36.5°C. being collected. t-Butylacetylene (10.6 g., 0.129 mole) was obtained in 12.9% yield.

A second run was carried out using a slightly modified procedure. The solid dichloride (98 g., 0.63 mole) was heated as before with a mixture of potassium hydroxide (390 g., 6.95 mole) and ethyleneglycol (250 c.c.). In this case, however, a stirrer was used to provide mixing when the mixture was hot and in a molten state. Liquid collected in the receiver was fractionated as before, the liquid boiling up to 36.5°C. being retained and that remaining being combined with the unsaturated chloride (27.6 g., 0.273 mole) and heated with a mixture of powdered potassium hydroxide (300 g., 5.36 mole) and ethyleneglycol (150 c.c.) as before. Liquid collected in the cooled receiver was then fractionated and liquid boiling up to 36.5°C. was collected. Finally the combined low boiling fractions were refractionated and liquid b.pt. 35.5-36.5°C. was collected. t-Butylacetylene (22.6 g., 0.275 mole) was obtained in 30.4% yield.

(ii). $2Na + 2NH_3 = 2NaNH_2 + H_2$.

$(CH_3)_3C\text{-}CCl_2\text{-}CH_3 + 3NaNH_2 = (CH_3)_3C\text{-}C{\equiv}CNa + 2NaCl + 3NH_3$.

$(CH_3)_3C\text{-}CCl = CH_2 + 2NaNH_2 = (CH_3)_3C\text{-}C{\equiv}CNa + NaCl + 2NH_3$.

$(CH_3)_3C\text{-}C{\equiv}CNa + H_2O = (CH_3)_3C\text{-}C{\equiv}CH + NaOH$.

As the previous preparations of t-butylacetylene had yielded only small amounts of product, a modification of the reaction used to prepare t-butylacetylenecarboxylic acid ($\underline{t}$-$C_4H_9C{\equiv}C$-COOH) via the sodium acetylide was attempted.[85] As this involved reaction in liquid ammonia with sodamide, an attempt was made to dry the 2:2-dichloro-3:3-dimethylbutane in order to keep losses of sodamide, via the reaction,

$$NaNH_2 + H_2O = NaOH + NH_3,$$

to a minimum. The presence of small amounts of water in the previous preparations were not critical, since some water was also produced by the reaction. An attempt to dry the solid dichloride by pumping, in vacuo, was not possible since it was found to be volatile. Some water was removed, however, by drying in a desiccator over phosphorus pentoxide. When the solid dichloride was dissolved in toluene a cloudy solution was produced, but addition of a small amount of anhydrous magnesium sulphate, followed by filtration, yielded a clear solution.

Sodium (71.5 g., 3.1 moles) was converted to sodamide using ferric nitrate, in the usual way, in liquid ammonia (1200 c.c.) in a 5-litre 3-necked flask fitted with, a dropping funnel, a stirrer with a nitrogen inlet, and a gas outlet leading to a Drechsel bottle containing heavy white oil arranged to keep air out of the system. The reaction vessel was maintained at ca. 40°C. by means of an acetone bath to which pieces of solid carbon dioxide were occasionally added. A mixture of 2:2-dichloro-3:3-dimethylbutane (80 g., 0.516 mole) and

2-chloro-3:3-dimethylbutene-1 (40 g., 0.338 mole) in toluene (200 c.c.) was added over 50 minutes. Stirring was continued for another hour and then the ammonia was allowed to boil off overnight. Residual ammonia was removed by heating the reaction vessel to 70°C. (30 minutes). The cooled reaction vessel contents were then hydrolysed by the addition of a saturated brine solution, volatile products being passed in turn through 2N sulphuric acid (1 litre), a tower containing calcium chloride and then condensed in two traps cooled to *ca.* -80°C. When about 1 litre of brine solution had been added and the vigorous reaction had moderated, the reaction vessel was heated to 100°C. (30 minutes). Liquid was collected in an empty flask, acting as a safety trap, next to the reaction vessel and also on the surface of the dilute sulphuric acid. This liquid (*ca.* 100 c.c.) was separated from water and dried over magnesium sulphate. Finally the dried liquid and that collected in the traps cooled to -80°C. was distilled through a column. A fraction b.pt. 37.2-37.8°C. was collected. *t*-Butylacetylene (42 g., 0.512 mole) was obtained in 60% yield. The acetylene was stored in a vacuum apparatus.

Preparation of *p*-Nitrophenylacetylene

i). $C_6H_5CH{=}CHCOOH + HNO_3 =$ *o*- and *p*-$NO_2C_6H_4CH{=}CHCOOH + H_2O$.

p-$NO_2C_6H_4CH{=}CHCOOC_2H_5 \leftarrow$ esterification ——

Cinnamic acid (50 g., 0.338 mole) was added in portions to fuming nitric acid (700 c.c.) at 0°C. with vigorous stirring (1 hour).[86] A voluminous precipitate formed rapidly after the addition of the first portion of cinnamic acid. After the addition of cinnamic acid was completed, the reaction mixture was allowed to warm up to room temperature and was stirred for 1 hour. The reaction mixture was then poured into cold water (2,000 c.c.) and the white nitrocinnamic acids were filtered off, and washed repeatedly with water to remove residual nitric acid. The mixture of o- and p-nitrocinnamic acids so obtained was then refluxed with alcohol (600 c.c.) containing concentrated sulphuric acid (30 c.c.), a clear yellow solution being obtained (2 hours reflux). On cooling pale yellow crystals of crude p-nitrocinnamic ethyl ester (25.8 g., 0.117 mole), which is much less soluble in cold alcohol than the ortho ester, were obtained in 35% yield (based on cinnamic acid). A sample recrystallised from alcohol melted at 138-140°C. (p-nitrocinnamic ethyl ester: m.pt. 138°C.[87]).

ii). $p\text{-}NO_2C_6H_4CH{=}CHCOOC_2H_5 + Br_2 = p\text{-}NO_2C_6H_4CHBr\text{-}CHBrCOOC_2H_5$

$$p\text{-}NO_2C_6H_4CHBr\text{-}CHBrCOOC_2H_5 + 3KOH = p\text{-}NO_2C_6H_4\ C{\equiv}C\text{-}COOK + 2KBr + C_2H_5OH + 2H_2O.$$

$$p\text{-}NO_2C_6H_4C{\equiv}C\text{-}COOK \xrightarrow[\text{boil } H_2O]{H_2SO_4} p\text{-}NO_2C_6H_4C{\equiv}CH + CO_2$$

The cinnamic ester (25.8 g., 0.117 mole) was pounded in a mortar with a slight excess of bromine (19.5 g., 6.5 c.c., 0.122 mole), a hard brown crust forming almost immediately. This was finely powdered and left in the air until the excess bromine had disappeared, leaving crude α-β-dibromo-p-nitrocinnamic ethyl ester (44.6 g.) in almost quantitative yield.[88] The dibromide was then dissolved in hot alcohol (50 c.c.) and hot potassium hydroxide (20 g., 0.357 mole) in alcohol (50 c.c.) was added slowly with stirring. A brown solution containing solid was produced. After boiling for 5 minutes the reaction mixture was left to stand (4 hours). The mixture was acidified with dilute sulphuric acid, diluted with water (400 c.c.), and filtered, yielding crude p-nitrophenylpropiolic acid.[88] A sample recrystallised from water melted at 180°C. (Beilstein: p-nitrophenylpropiolic acid, m.pt. 181°C; 198°C.). The acid so obtained was suspended in water (1000 c.c.) and then heated on a water-bath, under reflux, for 20 hours. Solid was filtered from the cooled solution, shaken with aqueous sodium carbonate and then refiltered. After washing with water, the brown solid was recrystallised from alcohol yielding pale yellow crystals of p-nitrophenylacetylide (4.5 g., 0.036 mole) in 26% yield (based on the amount of p-nitrocinnamic ethyl ester). The acetylide melted at 148-150°C., but a sample recrystallised again from alcohol melted at 152-153°C. (p-nitrophenylacetylene, m.pt. 152°C.[89]).

Preparation of Cuprous Chloride[90]

$$2CuCl_2 + Na_2SO_3 + 2H_2O = 2CuCl + 2NaHSO_4 + 2HCl.$$

A filtered solution of sodium sulphite ($Na_2SO_3.7H_2O$., 76 g., 0.301 mole) in water (250 c.c.) was added slowly with stirring to a filtered solution of cupric chloride ($CuCl_2.2H_2O$., 50 g., 0.264 mole) in water (50 c.c.). The precipitate of cuprous chloride settled readily leaving a green supernatant liquid. The mixture was then poured into a large volume of water (4 litres) containing sodium sulphite (10 g., 0.0396 mole) and concentrated hydrochloric acid (10 c.c.). After stirring for a few minutes, the solid was allowed to settle and the pale blue supernatant liquid was decanted carefully. Then the residual mixture was washed onto a sintered filter-plate which was connected to a water-pump, with dilute sulphurous acid. The solid was washed with glacial acetic acid (200 c.c.) in 50 c.c. portions. When the solid was only covered by a thin film of liquid the next portion of acid was added. This procedure was then repeated with three washings of absolute alcohol (3 x 100 c.c.) followed by six washings of anhydrous ether (6 x 50 c.c.). The solid was then sucked dry for about 30 seconds and dried in an oven at 80°C. for 20 minutes. The dry solid was then sealed in a glass tube. Cuprous chloride (23 g., 0.232 mole) was obtained as a slightly grey crystalline powder in 89.7% yield. Various quantities of cuprous chloride were made from time to time by this method, the yields of product being in the region of 85-90%.

Preparation of Triethylphosphine

$$C_2H_5Br + Mg = C_2H_5MgBr.$$

$$3C_2H_5MgBr + PBr_3 = (C_2H_5)_3P + 3MgBr_2.$$

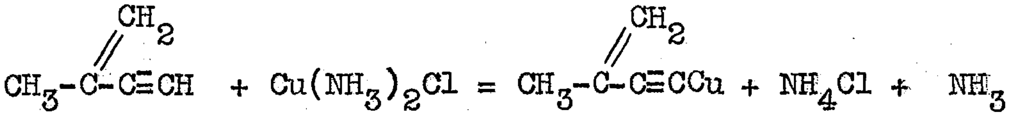
Magnesium (139 g., 5.7 mole), some of which was activated by heating with a crystal of iodine, was stirred with dry ether (1000 c.c.) in a 5-litre 3-necked flask fitted with, a dropping funnel, a stirrer with a nitrogen inlet and a reflux condenser. A solution of ethyl iodide (78 g., 0.5 mole) and ethyl bromide (562 g., 5.16 mole) in ether (500 c.c.) was added over 2 hours, allowing the ether to reflux gently. Reaction was completed by refluxing the reaction mixture on an isomantle for 1 hour. The reaction mixture was then cooled to ca. -15°C. by means of an acetone bath to which pieces of solid carbon dioxide were occasionally added. Phosphorus tribromide (406.5 g., 1.5 moles) in ether (1000 c.c.) was then added over 3 hours. The use of phosphorus bromide rather than the chloride facilitates stirring at this stage, because of the greater solubility of magnesium bromide in the reaction mixture. The reaction mixture was then allowed to warm up and was left to stand overnight, under nitrogen. The apparatus was then set up for distillation and connected to a 5-litre dropping funnel, acting as a receiver. Water (50 c.c.) was added slowly to the stirred reaction mixture, the heat of reaction causing ether to distil into the receiver. About one-sixth of a mole of a mixture of ammonium chloride and disodiumhydrogen phosphate ($Na_2HPO_4.2H_2O$) in water (100 c.c.) was then added. This solution was added to precipitate some of the magnesium in the form of the granular magnesium ammonium phosphate and thus facilitate the stirring of the solution. More water was added until the reaction moderated and then the reaction vessel was heated on an isomantle, the volume of the mixture being kept at ca. 2½ litres by adding water occasionally. A mixture of ether, triethylphosphine (dissolved in the ether) and water (ca. 500 c.c.) was collected in the receiver. The ether layer was separated and concentrated somewhat by distillation under nitrogen, dried over calcium sulphate and then distilled through a short vacuum-jacketed column. When the residual ether had distilled off, a liquid fraction b.pt. 123-127°C. was collected (triethylphosphine b.pt: 128°C.). Triethylphosphine (129 g., 1.09 mole) was obtained in 67.5% yield and stored in a 2-necked flask under nitrogen.

b) Reactions of iso-Propenylacetylene

Preparation of iso-Propenylcopperacetylide

Before carrying out reactions using the acetylenes prepared, some reactions of the copper derivative of the readily available iso-propenylacetylene were conveniently studied as a means of obtaining information with regard to the formation of co-ordination compounds of copper acetylides.

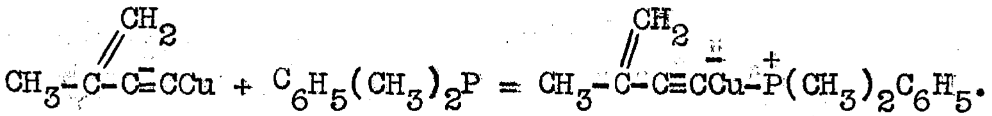
$$CuCl + 2NH_3 = Cu(NH_3)_2Cl.$$



$$CH_3-\overset{\overset{CH_2}{/\!/}}{C}-C\equiv CH + Cu(NH_3)_2Cl = CH_3-\overset{\overset{CH_2}{/\!/}}{C}-C\equiv CCu + NH_4Cl + NH_3$$

Cuprous chloride (14 g., 0.142 mole) was placed in a 500 c.c. 3-necked flask fitted with a dropping funnel, a reflux condenser, and a stopper. The flask was then evacuated and refilled with nitrogen and the procedure repeated. The stopper in the flask was then replaced by a stirrer, maintaining a flow of nitrogen so that air was excluded from the flask. Water (200 c.c.) was added to the cuprous chloride and sufficient concentrated ammonia (ca. 20 c.c.) to yield a clear, very pale blue solution, the colour being due to the presence of small amounts of the intensely blue $Cu(NH_3)_4^{++}$ ion caused by small amounts of oxygen in the apparatus. Addition of iso-propenylacetylene (9.0 g., 0.136 mole) in alcohol (100 c.c.) caused immediate precipitation of a bright yellow solid (30 minutes). The mixture was stirred for another 30 minutes and then the yellow solid was collected on a sintered filter-plate. After four washings with water the filtrate was colourless indicating removal of all soluble copper salts. The solid was then washed in turn with alcohol and acetone and dried, *in vacuo* (2 hours). *iso*-Propenylcopperacetylide (13.7 g., 0.107 mole) was obtained as a fine bright yellow powder in 78.5% yield and stored in a flask under nitrogen.

Reaction between *iso*-Propenylcopperacetylide and Phenyldimethylphosphine



$$CH_3-\overset{\overset{CH_2}{\|}}{C}-C\equiv CCu + C_6H_5(CH_3)_2P = CH_3-\overset{\overset{CH_2}{\|}}{C}-C\equiv C\overset{-}{Cu}-\overset{+}{P}(CH_3)_2C_6H_5.$$

The reaction between the copperacetylide and a phosphine was first studied, since it had been shown in other work carried out in these laboratories that the reaction between phenylcopperacetylide and triethylphosphine yielded the compound triethylphosphinecopper phenylacetylide[2]. Preliminary experiments showed that little if any reaction occurred between *iso*-propenylcopperacetylide and triphenylphosphine, since the copperacetylide remained undissolved in the benzene suspension, although reaction with phenyldimethylphosphine occurred rapidly.

iso-Propenylcopperacetylide (2 g., 0.0156 mole) was placed in one limb of a double Schlenk tube and the apparatus was filled with nitrogen. A mixture of phenyldimethylphosphine

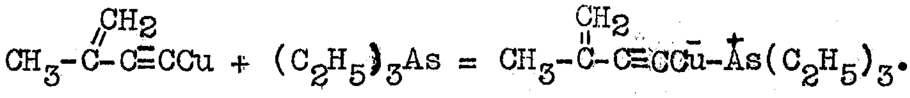
(2.2 g., 0.0159 mole) in benzene (20 c.c.) was added. Some heat was generated and the benzene solution became coloured red. As solid remained more benzene (10 c.c.) was added, but some solid still remained in suspension. However, addition of more phenyldimethylphosphine (2.2 g., 0.0156 mole) in benzene (10 c.c.) resulted in formation of a deep red, clear solution. The mixture was filtered into the other limb of the Schlenk tube and the benzene was removed, in vacuo, leaving a deep red viscous liquid, which contained small red crystals. Addition of n-hexane (30 c.c.) to the viscous liquid led to formation of a deep red solid. The liquid was therefore transferred to the other limb of the apparatus and cooled to ca. -80°C., but no solid was precipitated, although an oily liquid was produced. The n-hexane was therefore pumped off but only a small oily residue remained, this being dissolved in benzene and the solution removed by pipette. The red solid remaining in the Schlenk tube was dissolved in a mixture of benzene (15 c.c.) and methylcyclohexane (15 c.c.) at ca. 60°C. On cooling red crystals were obtained and the red supernatant liquid was filtered into the other limb of the apparatus. Solvent was removed, in vacuo, and a sample was analysed for carbon and hydrogen (Found: C, 51.40; H, 5.19. $C_{13}H_{16}CuP$ requires: C, 58.51; H, 6.05%).

As the amount of recrystallised material was small another similar quantity of the compound was made, two moles of phosphine to one of copperacetylide being used as before, since it was found that the equimolar mixture still contained material insoluble in benzene after standing overnight. The red material was recrystallised twice from a mixture of benzene and methyl*cyclo*hexane and analysed for carbon and hydrogen as before (Found: C, 50.20; H, 5.03%).

The red solid was found to decompose slowly in air, a white solid being produced in about two days.

Since this copperacetylide complex was not one of the main acetylenes to be studied in this research, and it appeared not easily purified, further work on the red compound was abandoned.

Reaction between *iso*-Propenylcopperacetylide and Triethylarsine



$$CH_3-\overset{\overset{CH_2}{/\!/}}{C}-C\equiv CCu + (C_2H_5)_3As = CH_3-\overset{\overset{CH_2}{\|}}{C}-C\equiv C\overset{-}{Cu}-\overset{+}{As}(C_2H_5)_3.$$

Initial tests using small amounts of the copperacetylide and triethylarsine in benzene showed that complex formation was slow. The suspension of the copperacetylide dissolved slowly on standing, especially with an excess of arsine present.

iso-Propenylcopperacetylide (2g., 0.014 mole) was suspended in benzene (10 c.c.), in a flask filled with nitrogen, and triethylarsine (12.7 g., 11 c.c., 0.078 mole) was added to the mixture, which was left to stand for 3 days, by which time a deep yellow solution containing a little solid had resulted. The reaction mixture was transferred to a double Schlenk tube filled with nitrogen and filtered through into the other limb. A slightly cloudy yellow solution was obtained. After pumping off solvent and excess triethylarsine, *in vacuo*, yellow solid remained. Tests on this solid showed that it was insoluble in benzene, methyl-*cyclo*-hexane, acetone, *n*-hexane and ether. In each case the yellow solid settled leaving a clear supernatant liquid. This suggested that the solid was probably *iso*-propenylcopperacetylide, since the co-ordination compound would be expected to be soluble in benzene and similar solvents. Samples of the solid were therefore washed with acetone and ether (to remove adhering triethylarsine) filtered and dried *in vacuo*. The samples were then analysed for copper by the copper thiocyanate method. (Found:- Cu, 37.60, 38.67. $C_{11}H_{20}AsCu$ requires: Cu, 21.86. C_5H_5Cu requires: Cu, 49.41%).

The values obtained were low for *iso*-propenylcopperacetylide although the insolubility of the yellow solid in organic solvents suggested that it was the impure copperacetylide. On the other hand the percentage of copper in the yellow solid was very high for the complex, and, since the stability of any complex formed with triethylarsine appeared to be small, work on this copperacetylide was concluded.

c) Reactions of Methylcopperacetylide

Preparation of Methylcopperacetylide

$$Cu(NH_3)_2Cl + CH_3\text{-}C\equiv CH = CH_3\text{-}C\equiv CCu + NH_3 + NH_4Cl$$

Cuprous chloride(16.4 g., 0.166 mole) was placed in a 500 c.c. 3-necked flask, fitted with a dropping funnel, a stirrer with a nitrogen inlet, and a cold-finger attached to the nitrogen outlet. The apparatus was filled with nitrogen as described previously. Water (200 c.c.) was then added to the cuprous chloride and sufficient concentrated ammonia (*ca*. 20 c.c.) to yield a clear, pale blue solution. This solution was kept cool by an ice-bath. A cold solution of methylacetylene (6.4 g., 0.161 mole) in absolute alcohol (75 c.c.) was added to the solution in the reaction vessel with vigorous stirring (10 minutes). Yellow solid formed immediately. The cold finger was maintained at *ca*. -80°C. in order to prevent loss of methylacetylene (b.pt. -23°C.) occurring. After stirring for 1½ hours the yellow solid was filtered off, washed with water until the filtrate was colourless, then washed in turn with alcohol and acetone and finally dried, *in vacuo* (2 hours). Methylcopperacetylide (15.5 g., 0.151 mole) was obtained as a bright yellow powder in 94% yield.

Samples of the yellow solid were analysed for copper by the copper thiocyanate method (Found: Cu, 61.81, 61.97. C_3H_3Cu requires Cu, 61.94%).

The Behaviour of Methylcopperacetylide with Various Donor Molecules

A series of reactions was studied in order to find which electron-donor compounds co-ordinate readily with methylcopperacetylide.

Samples of methylcopperacetylide (ca. 0.1 g., 9.7×10^{-4} mole) and toluene (ca. 2 c.c.) were placed in 2-necked flasks filled with nitrogen. The following series of reagents were then added to the various flasks:- phenyldimethylphosphine (2 molar equivalents), triphenylphosphine (2 molar equivalents), dipyridyl (1 molar equivalent), pyridine (2 molar equivalents), triethylamine (2 molar equivalents), ethylenethiourea (2 molar equivalents), diethyldithiolethylene (1 molar equivalent), triethylarsine (2 molar equivalents), and 9:10-phenanthroline (1 molar equivalent). In the cases of ethylenethiourea and 9:10-phenanthroline the reagent was not readily soluble in the toluene so more toluene (ca. 20 c.c.) was added and the flasks were warmed to ca. 60°C. Only in the case of phenyldimethylphosphine did a yellow colour form in the toluene, in all other cases, with the possible exception of the triphenylphosphine, where the toluene appeared to be slightly yellow, the toluene remained colourless and the acetylide remained undissolved. Thus from the compounds studied it appeared that phosphorus was the strongest donor element and co-ordinated most readily with the copper-acetylide.

Reaction between Methylcopperacetylide and Triethylphosphine

$$CH_3\text{-}C{\equiv}CCu + (C_2H_5)_3P = CH_3\text{-}C{\equiv}C\bar{C}u\text{-}\overset{+}{P}(C_2H_5)_3$$

Methylcopperacetylide (2 g., 0.0195 mole) was placed in one limb of a double Schlenk tube and the apparatus was filled with nitrogen. Toluene (25 c.c.) was then added, followed by triethylphosphine (2.4 g., 3 c.c., 0.024 mole) and the apparatus was shaken vigorously. After 15 minutes most of the copperacetylide had dissolved, a small amount of greenish solid being produced together with an oily liquid, which stuck to the sides of the apparatus. More triethylphosphine (0.4 g., 0.5 c.c., 3.4×10^{-3} mole) was added and the apparatus was shaken for another 15 minutes, by which time little solid remained. The solution was therefore filtered into the other limb of the Schlenk tube yielding a slightly cloudy yellow solution; some orange-yellow solid remained in the other limb. Solvent was pumped off, *in vacuo*, leaving yellow crystals, which were still slightly viscous. This material dissolved in *n*-hexane (15 c.c.), which on cooling to *ca.* -80°C. yielded a crystalline solid. Solvent was removed by filtration into the other limb of the Schlenk tube and the solid was recrystallised from more *n*-hexane. *n*-Hexane was removed by pumping, *in vacuo*, leaving pale yellow crystals in one limb of the Schlenk tube and viscous yellow material in the other. The recrystallised material was removed from the Schlenk tube to a 2-necked flask filled with nitrogen and weighed (1.1 g., ca. 25% yield of product assumed to be $CH_3C{\equiv}CCu.P(C_2H_5)_3$). A small sample of this material rapidly turned green on exposure to air so that it was necessary to store the product under nitrogen. It was found on attempting to recrystallise this solid from n-hexane that yellow solid was precipitated. The material was therefore transferred to a double Schlenk tube and the n-hexane solution was filtered into the other limb. White crystals were then obtained as described above. This material was then used for copper (page 88), carbon and hydrogen analyses (Found: Cu, 28.97, 28.92; C, 48.07; H, 8.23. $C_9H_{18}CuP$ requires: Cu, 28.78; C, 48.97; H, 8.22%).

The formation of the compound methylcopperacetylidetriethylphosphine, $\left[CH_3{-}C{\equiv}CCu.P(C_2H_5)_3\right]_n$, was thus confirmed.

An attempt was made to ascertain the degree of association, "n", from freezing point data in benzene. It was found however, that on addition of a sample of the complex to benzene that a fine yellow powder was precipitated. Addition of a small amount of triethylphosphine to the benzene then resulted in formation of a clear colourless solution. This indicated that the reaction,

$$CH_3{-}C{\equiv}CCu + (C_2H_5)_3P \rightleftharpoons CH_3{-}C{\equiv}CCu.P(C_2H_5)_3,$$

is an equilibrium reaction, the precipitation of the insoluble copperacetylide from solutions being suppressed in the presence of a small excess of triethylphosphine. Thus it was possible to carry out molecular weight determinations of samples of the complex using a benzene solvent containing <u>ca.</u> 1% of triethylphosphine:-

1.7204 g. of $CH_3C\equiv CCu.P(C_2H_5)_3$ was dissolved in 25 c.c. of benzene solution containing <u>ca.</u> 1% of triethylphosphine. The original volume of benzene/triethylphosphine solution used in the apparatus was 12 c.c.

a) Total volume of $CH_3C\equiv CCu.P(C_2H_5)_3$ sol. added to above = 3 c.c.

b) Total volume of $CH_3C\equiv CCu.P(C_2H_5)_3$ sol. added to above = 7 c.c.

c) Total volume of $CH_3C\equiv CCu.P(C_2H_5)_3$ sol. added to above = 11 c.c.

d) Total volume of $CH_3C\equiv CCu.P(C_2H_5)_3$ sol. added to above = 16 c.c.

a) Freezing point depression = ± 0.005°C. Mol. Wt. = ?
b) Freezing point depression = + 0.023°C. Mol. Wt. = 6,442.
c) Freezing point depression = + 0.058°C. Mol. Wt. = 3,316.
d) Freezing point depression = + 0.095°C. Mol. Wt. = 2,418.

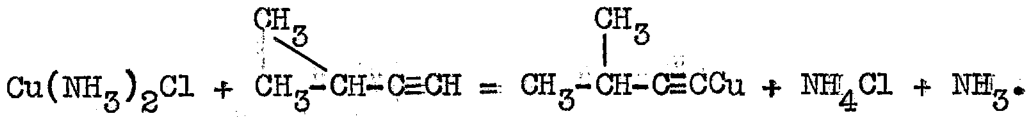
If the depressions of freezing point were measured from the previous addition of samples of the complex, the following intermediate values were obtained.

a)-b) Freezing point depression = +0.028°C. Mol. Wt. = 3,024
b)-c) Freezing point depression = +0.035°C. Mol. Wt. = 1,998
c)-d) Freezing point depression = +0.037°C. Mol. Wt. = 1,941

As the maximum depression for the most concentrated solution was only 0.095°C. the results obtained were not accurate. The results do however indicate that the complex is highly associated and that "n" $\gg$ 9.

d) Reactions with the Product from the iso-Propylacetylene Preparation

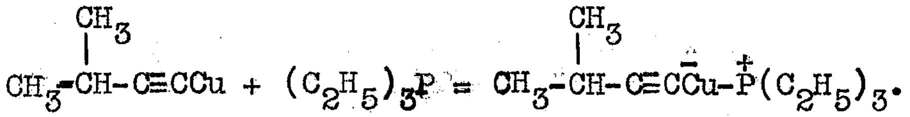
Attempted Preparation of iso-Propylcopperacetylide



$$\mathrm{Cu(NH_3)_2Cl + CH_3-\overset{CH_3}{CH}-C\equiv CH = CH_3-\overset{CH_3}{\overset{|}{C}H}-C\equiv CCu + NH_4Cl + NH_3.}$$

Cuprous chloride (16.4 g., 0.166 mole) was placed in a 500 c.c. 3-necked flask fitted with, a dropping funnel, a stirrer with a nitrogen inlet and a gas outlet, to which a cold-finger cooled to ca. -80°C. was attached to prevent loss of volatile material. The apparatus was filled with nitrogen, as described previously, and then water (200 c.c.) and sufficient concentrated ammonia (ca. 25 c.c.) was added to yield a clear solution. A solution of the product from the iso-propylacetylene preparation (11 g., 0.162 mole) in alcohol (75 c.c.) was then added, but no solid was precipitated although the solution became coloured a deep red-brown. As it was thought that the acetylene might be soluble in ammonia solutions, the reaction mixture was rendered neutral by the slow addition of 2.5N acetic acid (ca. 85 c.c.) as shown by universal indicator paper. Yellow solid was precipitated at this stage. This solid was filtered off, washed with water until the filtrate was colourless, then washed in turn with alcohol and acetone and dried in vacuo (2 hours). A fine yellowish powder (10 g., 0.076 mole) was obtained, a 47% yield of iso-propylcopperacetylide

Attempted Preparation of the Triethylphosphine Complex of iso-Propylcopperacetylide



$$CH_3-\overset{\overset{CH_3}{|}}{C}H-C{\equiv}CCu + (C_2H_5)_3P = CH_3-\overset{\overset{CH_3}{|}}{C}H-C{\equiv}C\overset{-}{C}u-\overset{+}{P}(C_2H_5)_3.$$

A sample of the solid (3 g., 0.023 mole) obtained from the previous reaction was placed in a double Schlenk tube filled with nitrogen. Benzene (25 c.c.) was added and triethylphosphine (3.2 g., 4 c.c., 0.027 mole). Heat was evolved and on shaking a yellow colour was developed in the benzene. After 1 hour solid still remained undissolved, but the benzene was filtered into the other limb of the Schlenk tube leaving orange solid behind. After removal of benzene by pumping, in vacuo (2 hours), a viscous yellow liquid remained. An attempt to crystallise this liquid by cooling was unsuccessful as also an attempt to crystallise a sample dissolved in n-hexane by cooling it to ca. -80°C. Samples of the liquid were then analysed for copper, which was weighed as the thiocyanate (Found: Cu, 19.68, 19.72. $C_{11}H_{22}CuP$ requires: Cu, 25.45%).

After standing for 3 days the viscous liquid began to crystallise and it was then possible to recrystallise the material from n-hexane by cooling the solution to ca.-80°C. The material was recrystallised three times and the almost white material was dried, in vacuo (2 hours), and stored under nitrogen. Samples of this material were then analysed for copper, carbon and hydrogen (Found: Cu, 19.91, 19.63; C, 42.98, 42.87; H, 8.96, 9.00. $C_{11}H_{22}CuP$ requires: Cu, 25.45; C, 53.09; H, 8.92%). As the copper content of the material remained unchanged after recrystallisation and the carbon content was low for the desired compound ($\underline{i}$-$C_3H_7C{\equiv}CCu.P(C_2H_5)_3$), it appeared that purification by recrystallisation could not readily be achieved.

The fact that a sample of the liquid from the attempted iso-propylacetylene preparation, did not yield a precipitate with alkaline potassium mercuri-iodide solution suggested that the substance was not in fact an acetylene. This formation of an insoluble mercuryacetylide derivative[76] is common to the simpler acetylenes which contain the group $-C{\equiv}CH$. Samples of the liquid were therefore analysed for carbon and hydrogen using a vacuum apparatus.

Each sample was measured out in a gas burette at constant volume. The gas was then sparked with an excess of oxygen, also measured at the same volume, in a combustion bulb. Condensable products (water and carbon dioxide) were collectedin a trap cooled by liquid nitrogen and the excess oxygen was transferred to the gas burette by means of a Töpler pump. The excess oxygen was then measured at the same volume as before. The condensed material was then allowed to warm up to the temperature of an acetone/solid carbon dioxide bath and the released carbon dioxide was measured in the gas burette as before. Since all pressure measurements were made at constant volume and at room temperature the amounts of gas were proportional to their pressures. Thus for a sample the following data were obtained:-

Pressure of sample = 2.285 cms.

Pressure of oxygen = 19.570 cms.

Pressure of excess oxygen after combustion = 5.824 cms.
Pressure of carbon dioxide formed = 8.993 cms.

Since,

$$C + O_2 = CO_2,$$

then the number of carbon atoms in the sample is $\frac{8.993}{2.285}$ or 3.93. The amount of oxygen used up in carbon dioxide formation was proportional to (19.570-8993) or 10.577 cms. Since a pressure of oxygen of 5.824 cms. remained then (10.577-5.824) or 4.753 cms. of oxygen equivalents must have been used up in formation of water. Now,

$$2H_2 + O_2 = 2H_2O,$$

therefore 4.753 cms. of oxygen are equivalent to 4x4.753 cms. or 19.012 cms. of hydrogen "atoms". Therefore the number of hydrogen atoms in the sample is 8.33.

Similarly, further analyses showed that the number of carbon atoms were 3.21 and 3.34 and the number of hydrogen atoms 6.62 and 6.91. The infra-red adsorption spectrum indicated that the iso-propyl group and acetylene group ($C \equiv C-H$) were present, but other peaks could not be satisfactorily accounted for. One peak indicated the presence of the olefinic group $-C=CH_2$, however, comparison with the spectrums of 3-methyl-1-butene, the isomeric 2-methyl-1-butene and 1:1 dimethylallene, possible products from the iso-propylacetylene preparation, showed that they did not fit the spectrum observed.

In view of the results obtained by analysis and the infra-red spectrum, it was concluded that the product from the iso-propylacetylene preparation consisted of a mixture of products. The non-formation of a mercury derivative suggested the absence of acetylene, which, however, contradicts the infra-red data. Further study of this liquid was therefore abandoned.

e) Reactions of t-Butylacetylene

Preparation of t-Butylcopperacetylide[91]

$$(CH_3)_3C\text{-}C{\equiv}CH + Cu(NH_3)_4Cl = (CH_3)_3C\text{-}C{\equiv}CCu + NH_4Cl + 3NH_3$$

Cuprous chloride (8.6 g., 0.087 mole) was placed in a 3-necked 500c.c. flask fitted with, a dropping funnel, a stirrer with a nitrogen inlet and a gas outlet fitted with a cold-finger cooled to ca. -80°C. in order to cut down losses of acetylene. The apparatus was filled with nitrogen as described previously. Concentrated ammonia (ca. 25 c.c.) and water (75 c.c.) was added yielding a pale blue solution. t-Butylacetylene (7 g., 0.085 mole) in alcohol (75 c.c.) was slowly added. Although red solid was formed, a layer of the acetylene floated on the surface of the water. After an hours stirring, however, this layer had disappeared and the reaction mixture was diluted by the addition of water (200c.c The solid was then filtered off, washed with 4N ammonia and water until a colourless filtrate was obtained and then dried, *in vacuo*. The dried solid was then extracted with cold benzene and the benzene solution was filtered from insoluble material (probably cuprous chloride), yielding a clear red solution. Removal of benzene, *in vacuo*, yielded the red modification of t-butylcopperacetylide (8.5 g., 0.059 mole) in 69% yield. From a second preparation using t-butylacetylene (25.7 g., 0.314 mole), t-butylcopperacetylide (26.4 g., 0.183

mole) was obtained in 58% yield. A sample of the solid was decomposed with concentrated nitric acid and silver nitrate was added. The absence of any turbidity indicated the absence of chloride, *i.e.*, absence of cuprous chloride.

Some of the copperacetylide was recrystallised from hot *n*-hexane and dried, *in vacuo*, yielding the orange-red modification of *t*-butylcopperacetylide. As the copper-acetylide appeared to be stable in air recrystallisations were carried out in stoppered flasks. A sample of the orange-red solid so obtained was then analysed volumetrically for copper (Found: Cu, 42.23. C_6H_9Cu requires:- Cu, 43.91%). As the result obtained was ra ther low some of the red-orange solid was again recrystallised from hot *n*-hexane. A sample of the dried material was then analysed for carbon and hydrogen. Another sample of the red-orange solid from the first recrystallisation was dissolved in ether, which was then cooled to *ca.* -80°C, when the yellow modification of *t*-butylcopperacetylide was obtained as a fine powder. Samples of this yellow material were analysed for copper, carbon and hydrogen.

	%Cu	%C	%H
Red-orange Sample	-	50.34	6.43
Yellow Sample	43.38	49.52	6.43
t-$C_4H_9C{\equiv}CCu$	43.91	49.79	6.27

Both red-orange and yellow modifications of *t*-butylcopperacetylide decomposed at 147-150°C. yielding a dark red viscous oil, which darkened on continued heating. The yellow form gradually turned orange on heating, this being noticeable at *ca.* 95°C., although the colour was still paler than that of the red-orange form just below the decomposition point.

Since this copperacetylide was soluble in organic solvents, unlike the other copperalkylacetylides, it was possible to carry out molecular weight determinations in benzene. The red modification of *t*-butylcopperacetylide was used, this being more soluble than the yellow form:-

t-Butylcopperacetylide (1.5795 g.) was dissolved in benzene (18 c.c.) of density 0.877 g./c.c.

The original volume of benzene used in the apparatus was 12 c.c.

a) Total volume of *t*-$C_4H_9C\equiv CCu$ sol. added to above = 4 c.c.
b) Total volume of *t*-$C_4H_9C\equiv CCu$ sol. added to above = 8 c.c.
c) Total volume of *t*-$C_4H_9C\equiv CCu$ sol. added to above = 12 c.c.
d) Total volume of *t*-$C_4H_9C\equiv CCu$ sol. added to above = 14.5 c.c.

a) Freezing point depression = 0.111°C. Mol. Wt. = 1,154.
b) Freezing point depression = 0.176°C. Mol. Wt. = 1,165.
c) Freezing point depression = 0.218°C. Mol. Wt. = 1,176.
d), Freezing point depression = 0.220°C. Mol. Wt. = 1,275.

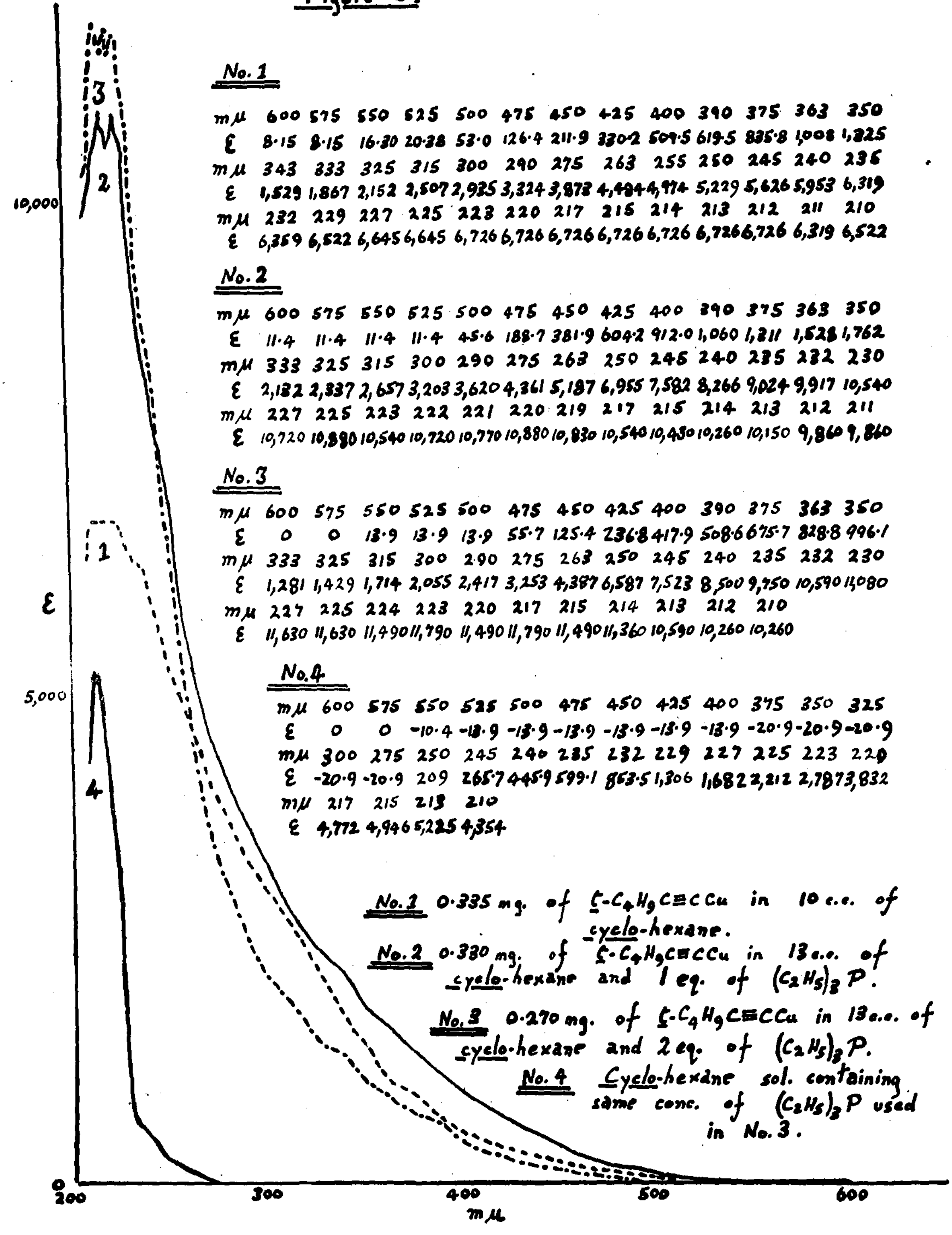
The last value recorded d) was not accurate since crystallisation of *t*-butylcopperacetylide occurred. The average molecular weight obtained from the first three results was 1,165. Since the molecular weight of t-butylcopperacetylide is 144.7, the degree of association in benzene is 8.05, i.e. n = 8, $[t\text{-}C_4H_9C\equiv CCu]_8$. This result was in accordance with those recorded by earlier workers.

Reaction between t-Butylcopperacetylide and Triethylphosphine

$$(CH_3)_3C\text{-}C\equiv C\text{-}Cu + (C_2H_5)_3P = (CH_3)_3C\text{-}C\equiv C\bar{C}u\text{-}\overset{+}{P}(C_2H_5)_3.$$

A sample of the orange-red form of t-butylcopperacetylide (2 g., 0.014 mole) was placed in one limb of a double Schlenk tube and the apparatus was filled with nitrogen. Benzene (30 c.c.) was added yielding an orange-red solution. Addition of triethylphosphine (1.68 g., 2 c.c., 0.014 mole) led to the formation of a pale yellow solution. Benzene was removed by pumping, in vacuo, and n-hexane (30 c.c.) was added to the yellow solid which remained forming a yellow solution. The solution was filtered into the other limb of the Schlenk tube. On cooling this solution to ca. -80°C. a whitish crystalline solid separated and the n-hexane was transferred into the other limb of the Schlenk tube. The solid was recrystallised from n-hexane and then the solvent was removed by pumping, in vacuo (2 hours), leaving pale yellow recrystallised solid in one limb of the Schlenk tube and yellow impure material in the other. Samples of the purified solid were then analysed for copper, carbon and

Figure 3.



No. 1

mμ	600	575	550	525	500	475	450	425	400	390	375	363	350
ε	8·15	8·15	16·30	20·38	53·0	126·4	211·9	330·2	509·5	619·5	835·8	1,008	1,325
mμ	343	333	325	315	300	290	275	263	255	250	245	240	236
ε	1,529	1,867	2,152	2,507	2,935	3,324	3,878	4,484	4,974	5,229	5,626	5,953	6,319
mμ	232	229	227	225	223	220	217	215	214	213	212	211	210
ε	6,359	6,522	6,645	6,645	6,726	6,726	6,726	6,726	6,726	6,726	6,726	6,319	6,522

No. 2

mμ	600	575	550	525	500	475	450	425	400	390	375	363	350
ε	11·4	11·4	11·4	11·4	45·6	188·7	381·9	604·2	912·0	1,060	1,311	1,528	1,762
mμ	333	325	315	300	290	275	263	250	245	240	235	232	230
ε	2,182	2,337	2,657	3,203	3,620	4,361	5,187	6,955	7,582	8,266	9,024	9,917	10,540
mμ	227	225	223	222	221	220	219	217	215	214	213	212	211
ε	10,720	10,880	10,540	10,720	10,770	10,880	10,830	10,540	10,450	10,260	10,150	9,860	9,860

No. 3

mμ	600	575	550	525	500	475	450	425	400	390	375	363	350
ε	0	0	13·9	13·9	13·9	55·7	125·4	236·8	417·9	508·6	675·7	828·8	996·1
mμ	333	325	315	300	290	275	263	250	245	240	235	232	230
ε	1,281	1,429	1,714	2,055	2,417	3,253	4,387	6,587	7,523	8,500	9,750	10,590	11,080
mμ	227	225	224	223	220	217	215	214	213	212	210		
ε	11,630	11,630	11,490	11,790	11,490	11,790	11,490	11,360	10,590	10,260	10,260		

No. 4

mμ	600	575	550	525	500	475	450	425	400	375	350	325
ε	0	0	-10·4	-13·9	-13·9	-13·9	-13·9	-13·9	-13·9	-20·9	-20·9	-20·9
mμ	300	275	250	245	240	235	232	229	227	225	223	220
ε	-20·9	-20·9	209	265·7	445·9	599·1	863·5	1,306	1,682	2,212	2,787	3,832
mμ	217	215	213	210								
ε	4,772	4,946	5,225	4,354								

No. 1 0·335 mg. of t-$C_4H_9C\equiv CCu$ in 10 c.c. of *cyclo*-hexane.

No. 2 0·330 mg. of t-$C_4H_9C\equiv CCu$ in 13 c.c. of *cyclo*-hexane and 1 eq. of $(C_2H_5)_3P$.

No. 3 0·270 mg. of t-$C_4H_9C\equiv CCu$ in 13 c.c. of *cyclo*-hexane and 2 eq. of $(C_2H_5)_3P$.

No. 4 *Cyclo*-hexane sol. containing same conc. of $(C_2H_5)_3P$ used in No. 3.

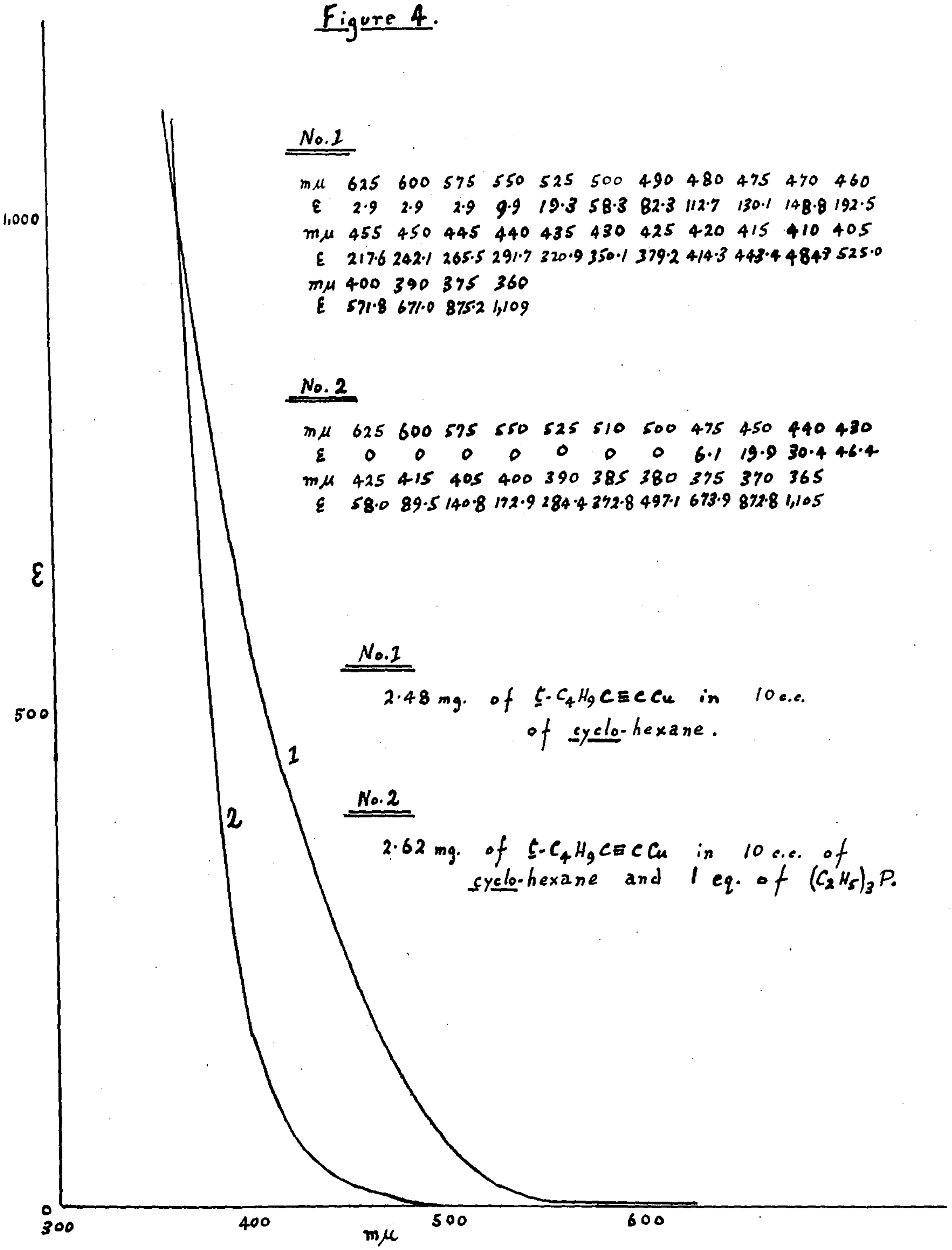
hydrogen (Found: Cu, 22.8; C, 48.53; H, 9.12. $C_{12}H_{24}CuP$ requires:- Cu, 24.18; C, 54.84; H, 9.20%).

Although both the copper and carbon values were low they suggested that the yellow material was the impure co-ordination complex.

As it seemed probable that preparation of the pure co-ordination compound might be difficult it was decided to detect such coördination via the adsorption spectrum of suitable mixtures of t-butylcopperacetylide and triethylphosphine in cyclo-hexane.

As the most probable co-ordination compound was expected to be one containing equimolar amounts of t-butylcopperacetylide and triethylphosphine, the adsorption spectrum of such a mixture in cyclo-hexane was first determined. A second solution containing two molar equivalents of triethylphosphine was determined similarly to see if further co-ordination occurred. Solutions of t-butylcopperacetylide and triethylphosphine in cyclo-hexane were also determined for comparison purposes. The results obtained were combined on one graph (fig. 3), the molecular extinction coefficient "ε" being plotted against the wavelength in millimicrons (mμ). The values of "ε" below ca. 230 mμ. were not accurate, because of the sensitivity of the instrument, so that it was not possible to draw any definite conclusions from the composite graph obtained, although it appeared that only a 1:1 co-ordination com-

Figure 4.



No. 1

mμ	625	600	575	550	525	500	490	480	475	470	460
ε	2·9	2·9	2·9	9·9	19·3	58·3	82·3	112·7	130·1	148·8	192·5
mμ	455	450	445	440	435	430	425	420	415	410	405
ε	217·6	242·1	265·5	291·7	320·9	350·1	379·2	414·3	443·4	484·7	525·0
mμ	400	390	375	360							
ε	571·8	671·0	875·2	1,109							

No. 2

mμ	625	600	575	550	525	510	500	475	450	440	430
ε	0	0	0	0	0	0	0	6·1	19·9	30·4	46·4
mμ	425	415	405	400	390	385	380	375	370	365	
ε	58·0	89·5	140·8	172·9	284·4	372·8	497·1	673·9	872·8	1,105	

No. 1

2·48 mg. of *t*-$C_4H_9C\equiv CCu$ in 10 c.c. of *cyclo*-hexane.

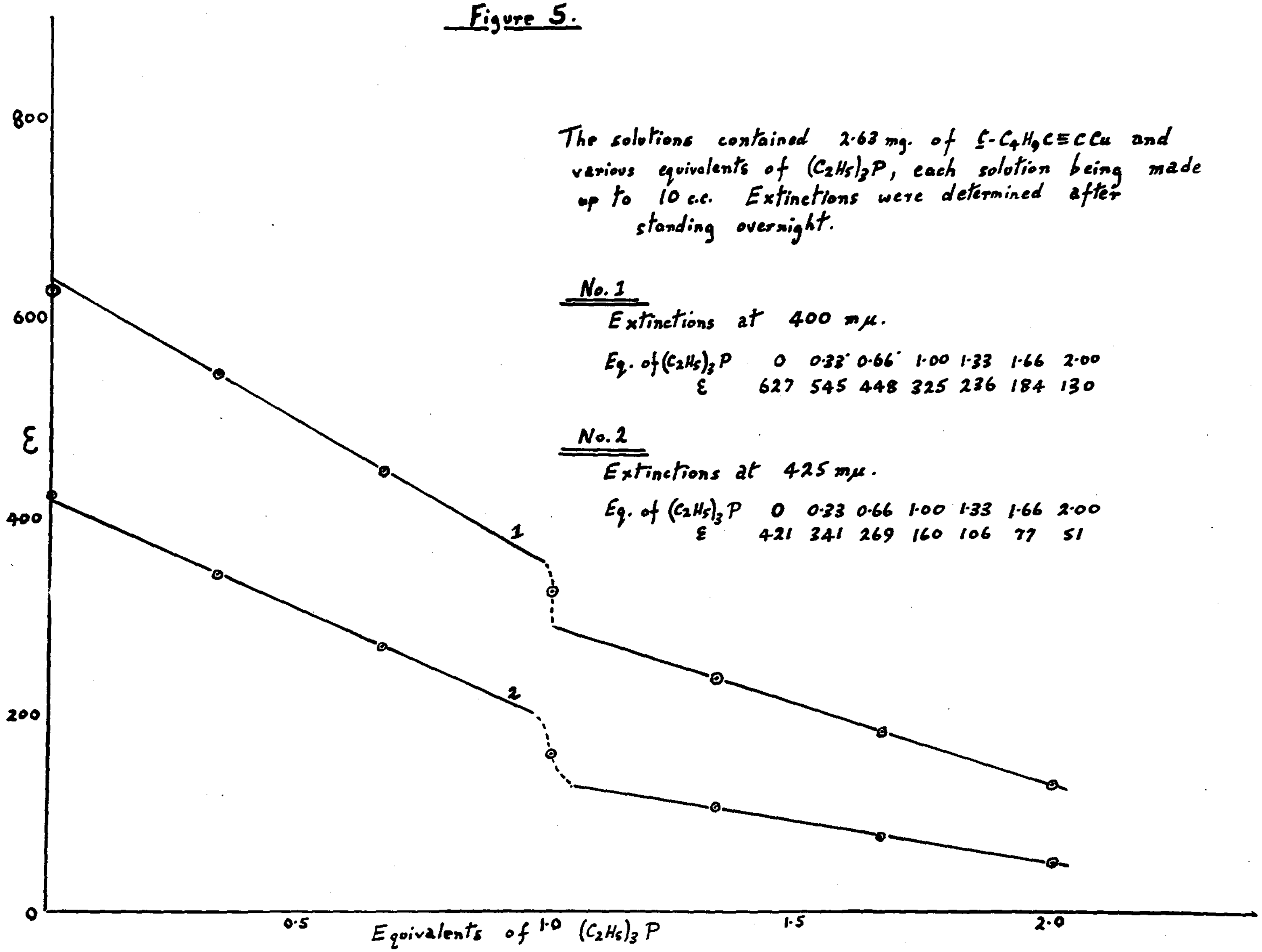
No. 2

2·62 mg. of *t*-$C_4H_9C\equiv CCu$ in 10 c.c. of *cyclo*-hexane and 1 eq. of $(C_2H_5)_3P$.

pound formed. It was also noted that although addition of triethylphosphine to t-butylcopperacetylide, in a suitable solvent, caused a change of colour from orange to yellow (a decrease in adsorption at longer wavelengths), the graph (fig. 3) showed that the solution containing a equimolar mixture of t-butylcopperacetylide and triethylphosphine possessed a higher extinction than a solution of t-butylcopperacetylide. This phenomenon was investigated further at higher wavelengths using more concentrated solutions. The graph obtained (fig. 4) showed clearly an initial decrease in the adsorption of the solution containing triethylphosphine, so that it was concluded that the first results were not accurate, the discrepancy noted probably being due to weighing errors incurred in making up the dilute solutions. It was also found that the reaction between t-butylcopperacetylide and triethylphosphine was only completed after standing overnight (the adsorption of mixtures changed on standing, but became steady after standing overnight) in the more concentrated solutions, so that errors due to this slow reaction were probably also incurred in the initial experiments, since the adsorption of the t-butylcopperacetylide and triethylphosphine solutions were determined after standing ca. 2 hours.

The number of molecules of triethylphosphine co-ordinating with a molecule of t-butylcopperacetylide was shown by determining the molecular extinction coefficient of solutions

Figure 5.



The solutions contained 2·63 mg. of $\underline{t}$-$C_4H_9C\equiv CCu$ and various equivalents of $(C_2H_5)_3P$, each solution being made up to 10 c.c. Extinctions were determined after standing overnight.

No. 1

Extinctions at 400 mμ.

Eq. of $(C_2H_5)_3P$	0	0·33	0·66	1·00	1·33	1·66	2·00
ε	627	545	448	325	236	184	130

No. 2

Extinctions at 425 mμ.

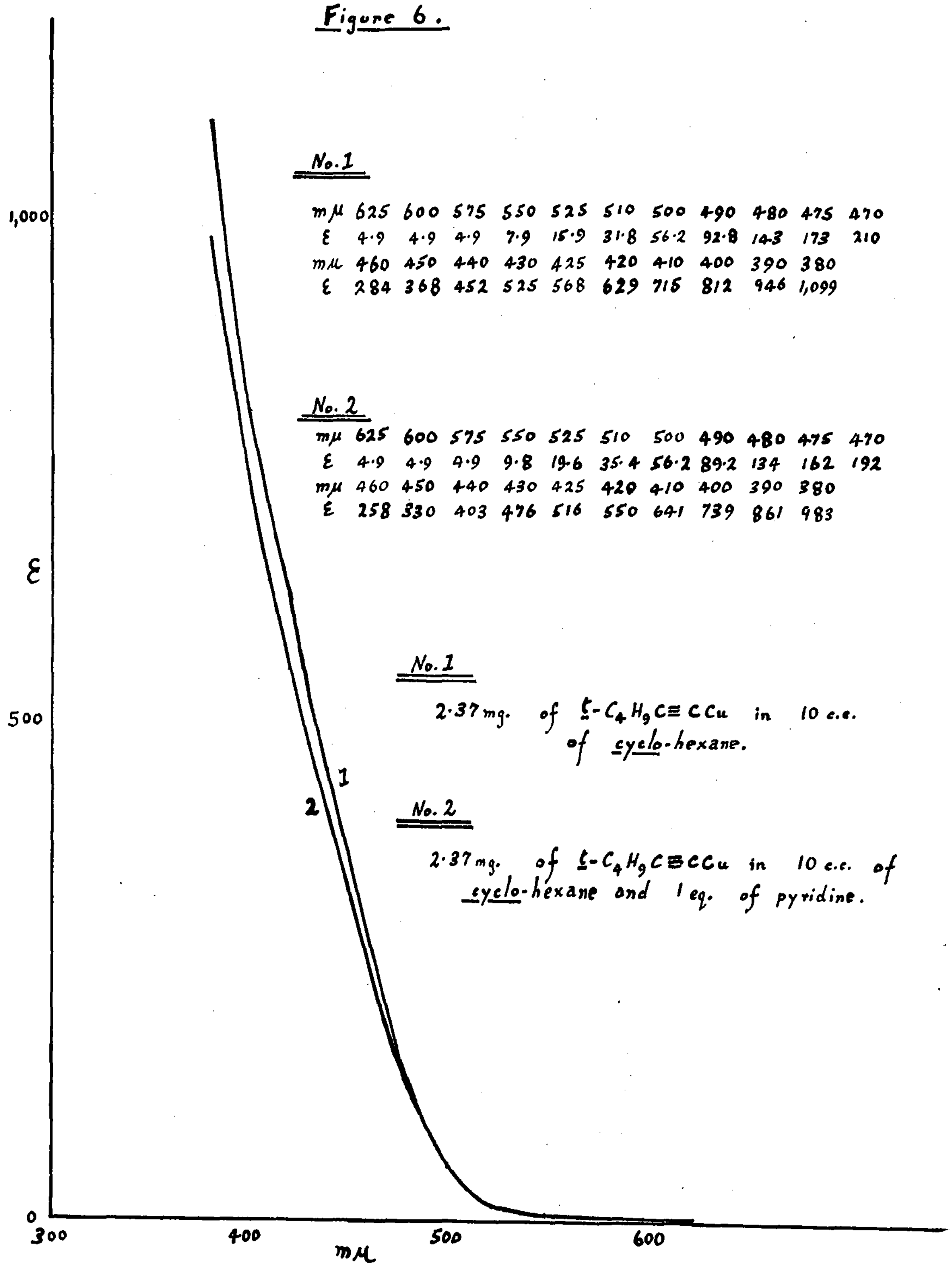
Eq. of $(C_2H_5)_3P$	0	0·33	0·66	1·00	1·33	1·66	2·00
ε	421	341	269	160	106	77	51

of *t*-butylcopperacetylide containing various amounts of triethylphosphine at a constant wavelength. Each solution contained the same weight of *t*-butylcopperacetylide and was made up to the same volume, all the mixtures being allowed to stand overnight before their adsorptions were determined. The second graph (fig. 4) showed that the greatest change in adsorption between a solution of *t*-butylcopperacetylide containing triethylphosphine and one of *t*-butylcopperacetylide occurred at *ca.* 400 $m\mu$. Adsorptions were therefore carried out at 400 $m\mu$ and 425 $m\mu$. A graph (fig. 5) of molecular extinction coefficient against number of equivalents of phosphine was then plotted. From the graph it can be seen that there is an abrupt change in the adsorption for the solution containing equi-molar amounts of triethylphosphine and *t*-butylcopper-acetylide. Thus it appeared that a 1:1 co-ordination complex was formed as indicated previously. The decrease of adsorption for solutions containing over one equivalent of triethylphosphine suggested that the co-ordination compound dissociated in solution, i.e.,

$$\underline{t}\text{-C}_4\text{H}_9\text{C}\equiv\text{C}\overset{-}{\text{Cu}}\text{-}\overset{+}{\text{P}}(\text{C}_2\text{H}_5)_3 \rightleftharpoons \underline{t}\text{-C}_4\text{H}_9\text{C}\equiv\text{CCu} + \text{P}(\text{C}_2\text{H}_5)_3.$$

The excess triethylphosphine drives the equilibrium towards the formation of the co-ordination compound, which adsorbs less strongly than *t*-butylcopperacetylide in this region, thus producing the decrease in adsorption observed.

Figure 6.



No. 1

mμ	625	600	575	550	525	510	500	490	480	475	470
ε	4·9	4·9	4·9	7·9	15·9	31·8	56·2	92·8	143	173	210
mμ	460	450	440	430	425	420	410	400	390	380	
ε	284	368	452	525	568	629	715	812	946	1,099	

No. 2

mμ	625	600	575	550	525	510	500	490	480	475	470
ε	4·9	4·9	4·9	9·8	19·6	35·4	56·2	89·2	134	162	192
mμ	460	450	440	430	425	420	410	400	390	380	
ε	258	330	403	476	516	550	641	739	861	983	

No. 1

2·37 mg. of t-$C_4H_9C\equiv CCu$ in 10 c.c. of *cyclo*-hexane.

No. 2

2·37 mg. of t-$C_4H_9C\equiv CCu$ in 10 c.c. of *cyclo*-hexane and 1 eq. of pyridine.

Figure 7.

The solutions contained 2·37 mg. of t-$C_4H_9C\equiv CCu$ and various equivalents of pyridine, each solution being made up to 10 c.c. Extinctions were determined after standing overnight.

No. 1

Extinctions at 400 mμ.

Eq. of Pyridine	0	0·33	0·66	1·00	1·33	1·66	2·00
ε	812	751	751	739	739	782	757

No. 2

Extinctions at 390 mμ.

Eq. of Pyridine	0	0·33	0·66	1·00	1·33	1·66	2·00
ε	946	873	879	861	861	898	879

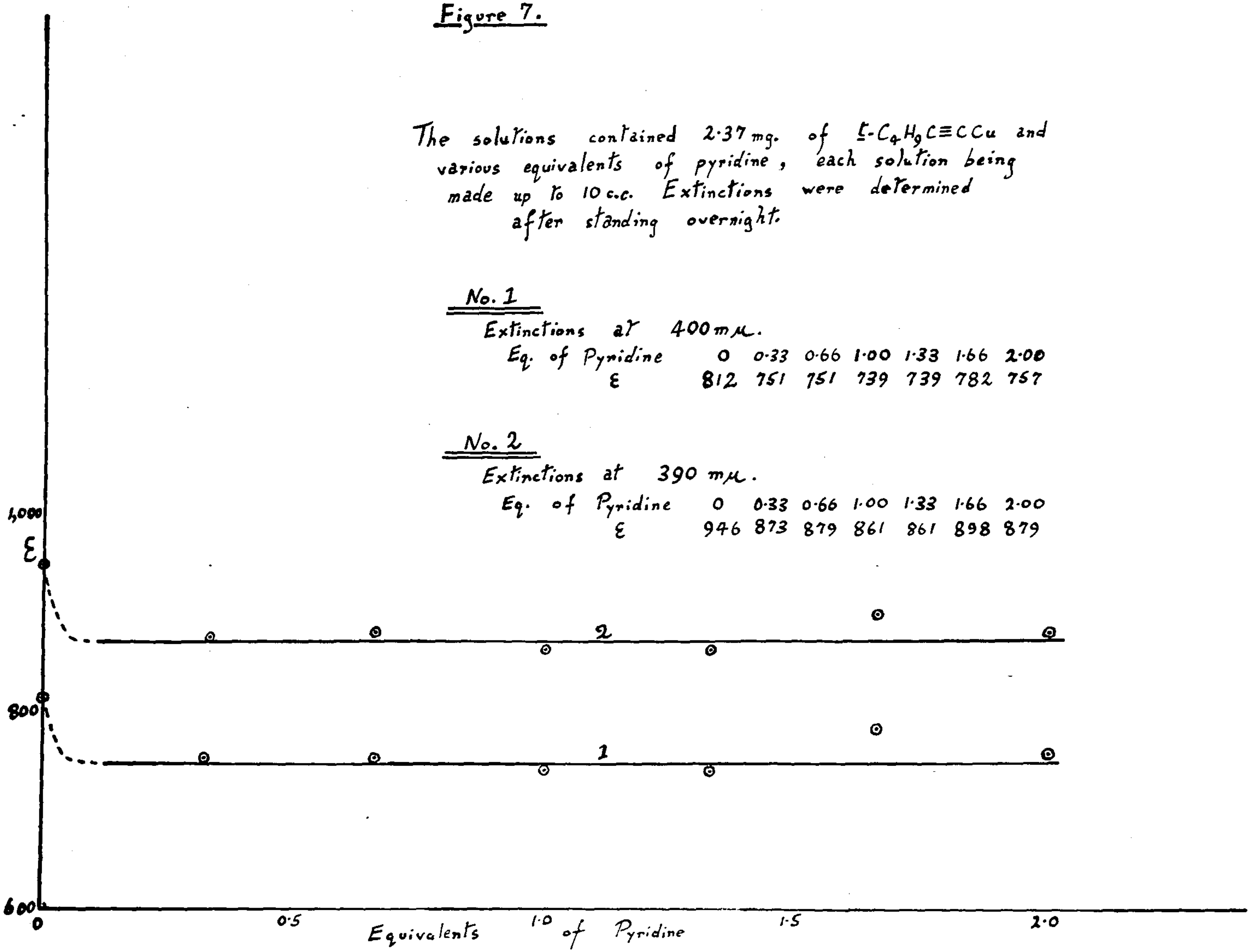
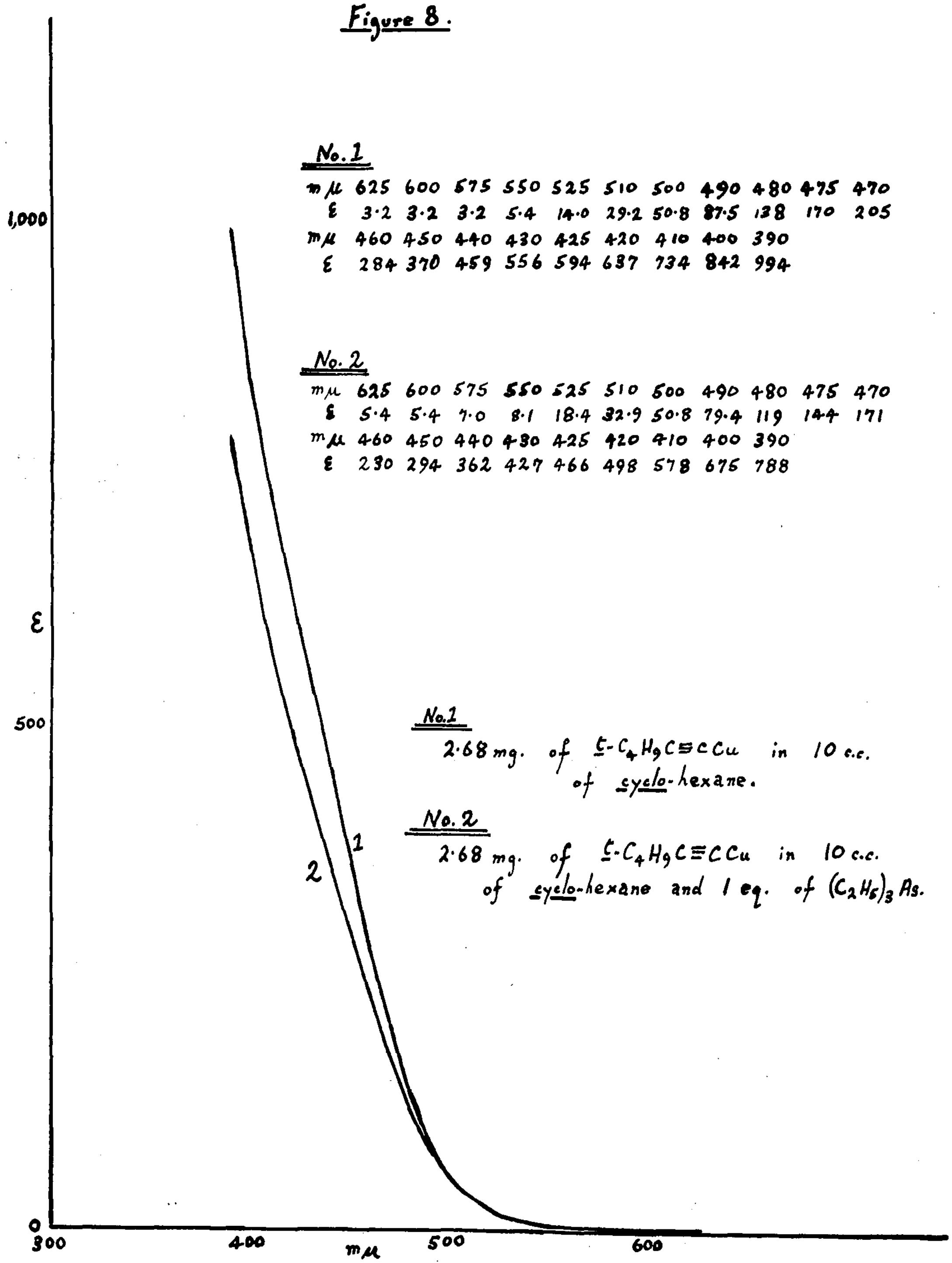


Figure 8.



No. 1

mμ	625	600	575	550	525	510	500	490	480	475	470
ε	3·2	3·2	3·2	5·4	14·0	29·2	50·8	87·5	138	170	205
mμ	460	450	440	430	425	420	410	400	390		
ε	284	370	459	556	594	637	734	842	994		

No. 2

mμ	625	600	575	550	525	510	500	490	480	475	470
ε	5·4	5·4	7·0	8·1	18·4	32·9	50·8	79·4	119	144	171
mμ	460	450	440	430	425	420	410	400	390		
ε	230	294	362	427	466	498	578	675	788		

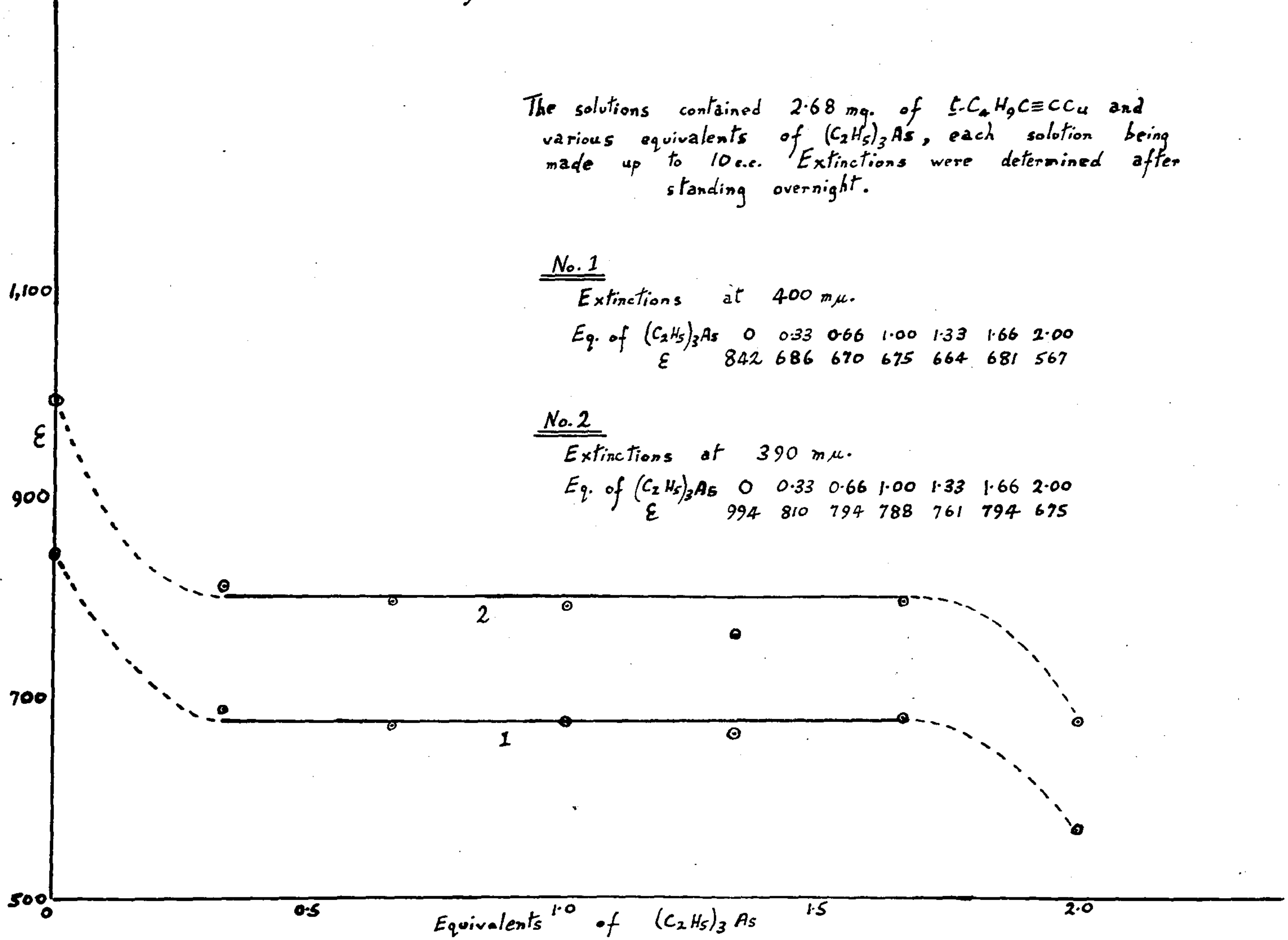
No. 1

2·68 mg. of *t*-$C_4H_9C{\equiv}CCu$ in 10 c.c. of *cyclo*-hexane.

No. 2

2·68 mg. of *t*-$C_4H_9C{\equiv}CCu$ in 10 c.c. of *cyclo*-hexane and 1 eq. of $(C_2H_5)_3As$.

Figure 9.



The solutions contained 2·68 mg. of $\underline{t}$-$C_4H_9C{\equiv}CCu$ and various equivalents of $(C_2H_5)_3As$, each solution being made up to 10 c.c. Extinctions were determined after standing overnight.

No. 1

Extinctions at 400 mμ.

Eq. of $(C_2H_5)_3As$	0	0·33	0·66	1·00	1·33	1·66	2·00
ε	842	686	670	675	664	681	567

No. 2

Extinctions at 390 mμ.

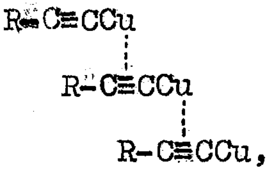
Eq. of $(C_2H_5)_3As$	0	0·33	0·66	1·00	1·33	1·66	2·00
ε	994	810	794	788	761	794	675

The Behaviour of t-Butylcopperacetylide with Various Donor Elements

Initial experiments with *t*-butylcopperacetylide showed that it dissolved in diethylamine but not pyridine. Benzene solutions of the acetylide became paler in colour on addition of triethylarsine. Removal of benzene yielded a viscous yellow material, which would not dissolve readily in ether or *n*-hexane.

As the study of the adsorption of mixtures of *t*-butylcopperacetylide and triethylphosphine indicated that a co-ordination compound formed, similar experiments were carried out with pyridine and triethylarsine (Figs. 6-9). From the graphs obtained it appeared that there was no indication of the formation of any definite co-ordination compound. There was no abrupt drop in the extinction of the solution containing equimolar amounts of *t*-butylcopperacetylide and the donor compound. An initial drop in the extinction appeared to occur on addition of either pyridine and triethylarsine to the *t*-butylcopperacetylide.

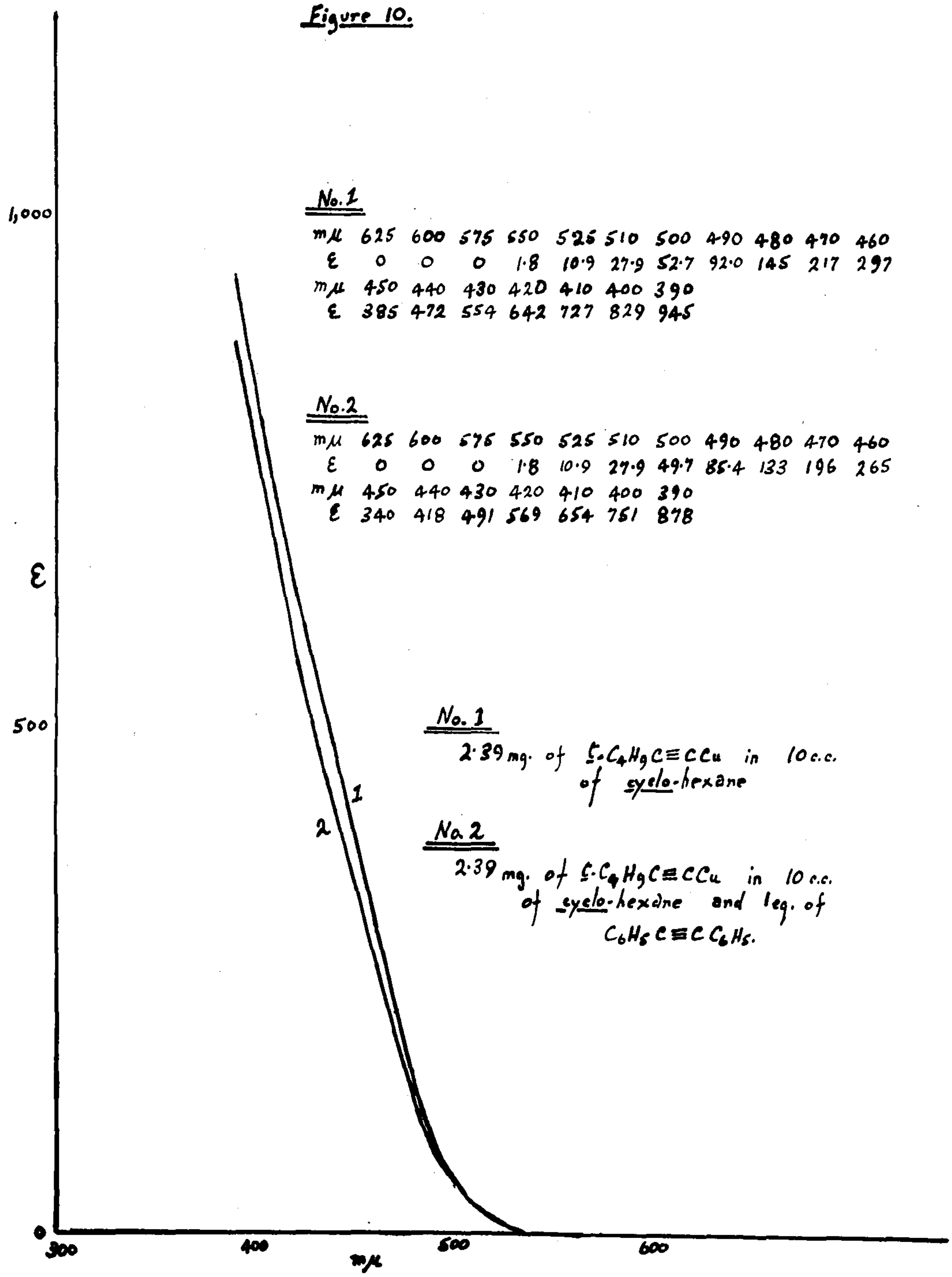
As it was thought that co-ordination of the copper in the acetylide might occur with the acetylene grouping, *i.e.*,



$$\begin{array}{lll} R-C\equiv CCu & & \\ \quad\;\vdots & & \\ & R-C\equiv CCu & \\ & \quad\;\vdots & \\ & & R-C\equiv CCu, \end{array}$$

adsorption experiments of *t*-butylcopperacetylide solutions containing various amounts of diphenyldiacetylene were carried out. Again there was no

Figure 10.



No. 1

mμ	625	600	575	550	525	510	500	490	480	470	460
ε	0	0	0	1·8	10·9	27·9	52·7	92·0	145	217	297

mμ	450	440	430	420	410	400	390
ε	385	472	554	642	727	829	945

No. 2

mμ	625	600	575	550	525	510	500	490	480	470	460
ε	0	0	0	1·8	10·9	27·9	49·7	85·4	133	196	265

mμ	450	440	430	420	410	400	390
ε	340	418	491	569	654	761	878

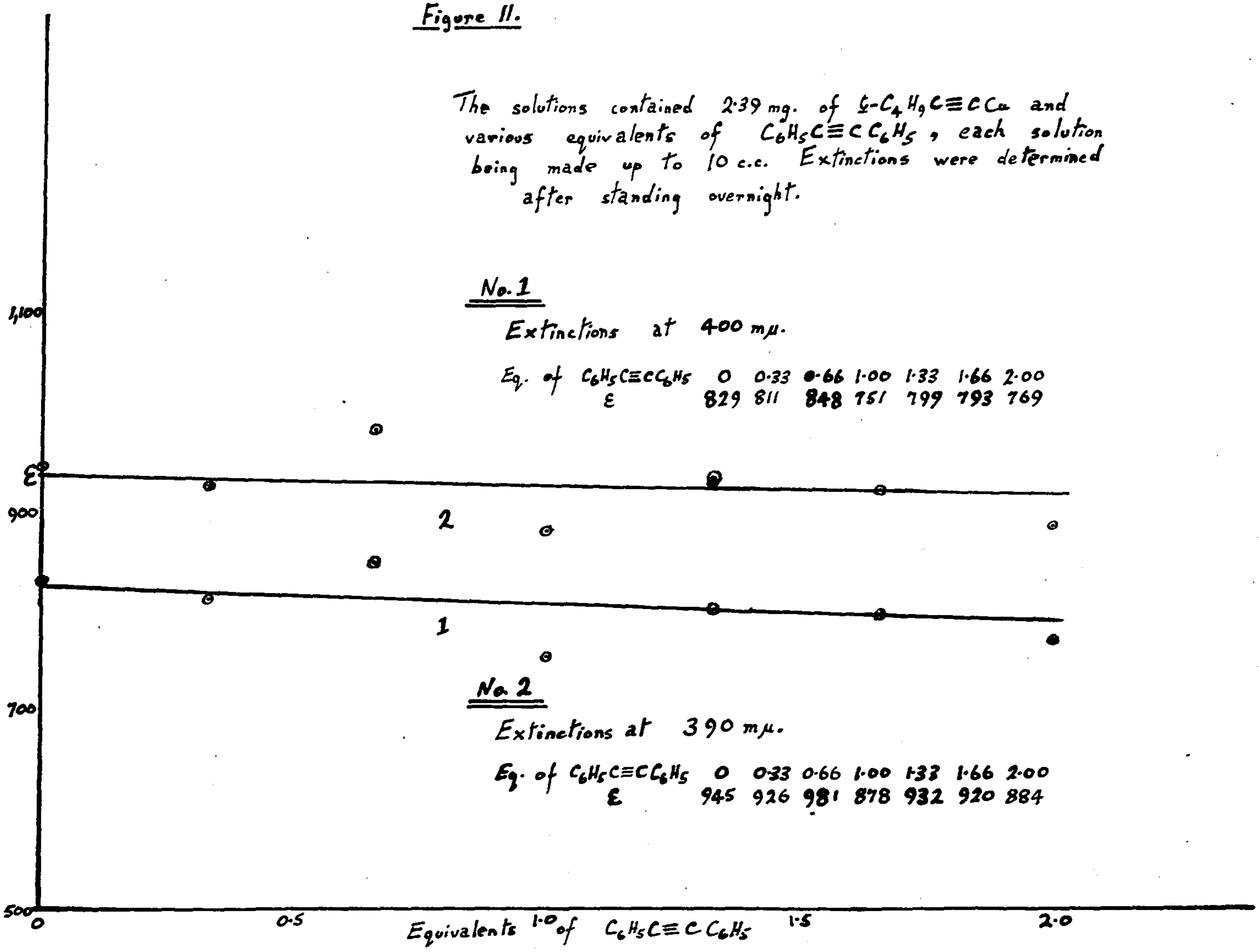
No. 1

2·39 mg. of t-$C_4H_9C\equiv CCu$ in 10 c.c. of cyclo-hexane

No. 2

2·39 mg. of t-$C_4H_9C\equiv CCu$ in 10 c.c. of cyclo-hexane and 1 eq. of $C_6H_5C\equiv CC_6H_5$.

Figure II.



The solutions contained 2·39 mg. of $t\text{-}C_4H_9C\equiv CCu$ and various equivalents of $C_6H_5C\equiv CC_6H_5$, each solution being made up to 10 c.c. Extinctions were determined after standing overnight.

No. 1

Extinctions at 400 mμ.

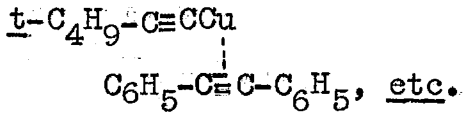
Eq. of $C_6H_5C\equiv CC_6H_5$	0	0·33	0·66	1·00	1·33	1·66	2·00
ε	829	811	848	751	799	793	769

No. 2

Extinctions at 390 mμ.

Eq. of $C_6H_5C\equiv CC_6H_5$	0	0·33	0·66	1·00	1·33	1·66	2·00
ε	945	926	981	878	932	920	884

indication of formation of a definite co-ordination complex, although the graphs obtained (Figs. 10-11) showed a gradual drop in extinction as diphenylacetylene was added. Such a phenomenon might be attributable to weak co-ordination of the acetylene group of diphenylacetylene with some of the copper atoms from the acetylide, i.e.,



$$\begin{array}{l} \underline{t}\text{-}C_4H_9\text{-}C\equiv CCu \\ \qquad\qquad\qquad\vdots \\ \qquad\quad C_6H_5\text{-}C\equiv C\text{-}C_6H_5,\ \text{etc.} \end{array}$$

f) Reactions with Phenylcopperacetylide

Reaction between Phenylcopperacetylide and Triethylphosphine

$$C_6H_5C\equiv CCu + (C_2H_5)_3P = C_6H_5C\equiv C\bar{C}u-\overset{+}{P}(C_2H_5)_3$$

The compound resulting from the reaction between phenylcopperacetylide and triethylphosphine was first prepared in other work carried out in these laboratories.[2] Analysis show that the compound was $\left[C_6H_5C\equiv CCu.P(C_2H_5)_3\right]_n$.

Phenylcopperacetylide (10g., 0.016 mole) was suspended in benzene (50 c.c.) in a double Schlenk tube, under nitrogen. Triethylphosphine (8.8 g., 11 c.c., 0.093 mole) was added in two equal portions. After shaking for *ca.* 30 minutes most of the solid had dissolved producing a deep yellow solution. The solution was heated to *ca.* 60°C. and filtered into the other limb of the Schlenk tube, leaving behind a small amount of yellowish solid. Benzene was removed by pumping, *in vacuo*. The yellow solid remaining was dissolved in hot *n*-hexane, which wa allowed to cool to room temperature and was then cooled to *ca.* -80°C, the recrystallised solid being collected on the sintered plate of the double Schlenk tube. This material was again recrystallised from *n*-hexane and the solid dried, *in vacuo*. Yellow needles of the purified product were obtained (9 g. 0.032 mole, 52% yield).

A sample of the co-ordination compound was exposed to air over 2 days before turning green in colour (*cf.*

methylcopperacetylidetriethylphosphine compound, page 48). Phenylcopperacetylidetriethylphosphine melted at 138.5-139.5°C., with some decomposition, the melt turning slightly brown in colour.

The degree of association of the compound "n" was ascertained by molecular weight measurements in benzene and nitrobenzene:-

2.200 g. of $C_6H_5C\equiv CCu.P(C_2H_5)_3$ were dissolved in benzene (20 c.c.)
The original volume of benzene in the apparatus was 12 c.c.

a) Total volume of $C_6H_5C\equiv CCu.P(C_2H_5)_3$ sol. added to above= 4 c.c
b) Total volume of $C_6H_5C\equiv CCu.P(C_2H_5)_3$ sol. added to above= 8 c.c
c) Total volume of $C_6H_5C\equiv CCu.P(C_2H_5)_3$ sol. added to above =12 c.c
d) Total volume of $C_6H_5C\equiv CCu.P(C_2H_5)_3$ sol. added to above=16 c.c

a) Freezing point depression = +0.149°C. Mol. Wt. = 1,077.
b) Freezing point depression = +0.277°C. Mol. Wt. = 927.
c) Freezing point depression = +0.318°C. Mol. Wt. = 1,010.
d) Freezing point depression = +0.385°C. Mol. Wt. = 953.

1.857 g. of $C_6H_5C\equiv CCu.P(C_2H_5)_3$ were dissolved in benzene (20 c.c.)
The original volume of benzene in the apparatus was 12 c.c.

e) Total volume of $C_6H_5C\equiv CCu.P(C_2H_5)_3$ sol. added to above = 4cc
f) Total volume of $C_6H_5C\equiv CCu.P(C_2H_5)_3$ sol. added to above = 8cc
g) Total volume of $C_6H_5C\equiv CCu.P(C_2H_5)_3$ sol. added to above =11.5cc

e) Freezing point depression = +0.130°C. Mol. Wt. = 1,042.
f) Freezing point depression = +0.223°C. Mol. Wt. = 972.
g) Freezing point depression = +0.263°C. Mol. Wt. = 1,009.

From the results obtained the degree of association of the compound, $C_6H_5C{\equiv}CCu.P(C_2H_5)_3$, in freezing benzene is "n" = 3.8, 3.3, 3.6, 3.4, 3.7, 3.4, 3.6 at 0.097, 0.158, 0.197, 0.222, 0.082, 0.131, 0.161M.

1.692 g. of $C_6H_5C{\equiv}C.P(C_2H_5)_3$ were dissolved in nitrobenzene (20 c.c.), a deep-red solution being produced. The original volume of benzene in the solution was 12 c.c.

h) Total volume of $C_6H_5C{\equiv}CCu.P(C_2H_5)_3$ sol. added to above = 5c
i) Total volume of $C_6H_5C{\equiv}CCu.P(C_2H_5)_3$ sol. added to above = 10c
j) Total volume of $C_6H_5C{\equiv}CCu.P(C_2H_5)_3$ sol. added to above = 15c

h) Depression of freezing point = +0.215°C. Mol. Wt. = 663.
i) Depression of freezing point = +0.270°C. Mol. Wt. = 816.
j) Depression of freezing point = +0.306°C. Mol. Wt. = 880.

The results obtained from nitrobenzene show an increase in molecular weight with increasing concentration.

From the results obtained from freezing nitrobenzene the degree of association of the compound is "n" = 2.3, 2.9, 3.1 at 0.088, 0.136, 0.166M. An a ttempt to obtain the molecular weight of the compound in boiling ether was abandoned, since yellow solid formed on heating.

Molar polarisation measurements carried out in other work in these laboratories[92] indicated that the total polarisation was small (*ca.* 125 c.c./mole). In view of the lack of data for molar refractions of some of the bonds (copper-phosphorus, copper-carbon), and the fact that the compound adsorbed in the visible region, it was not possible to ascertain the electron polarisation accurately. However, the measurement obtained indicated that the dipole moment (*ca.* 1.40) was small as expected for such an associated compound.

The Behaviour of Phenylcopperacetylide with Various Donor Compounds

Phenylcopperacetylide did not dissolve in cold or hot triethylamine. The copperacetylide was insoluble in cold pyridine, but dissolved in hot, producing a black solution. Addition of cold piperidine to phenylcopperacetylide led to formation of a dark green solution, which turned brown on warming. The copperacetylide also dissolved in *iso*-propylamine. A sample was extracted with boiling *iso*-propylamine under nitrogen Yellow solid formed in the *iso*-propylamine, which turned black on standing. The yellow solid was not soluble in ether or benzene, *i.e.*, phenylcopperacetylide.

A sample of phenylcopperacetylide was found to react slowly with triethylarsine in benzene, producing a pale yellow solution. The copperacetylide reacted slowly with *o*-phenylene-*bis*-dimethylarsine, a pale yellow solution being produced (ca. 5 hours). Addition of benzene led to formation of a cloudy solution. When, however, the benzene was removed by pumping, in vacuo, white crystals were slowly deposited from the excess of the diarsine. There was no opportunity to follow this observation any further.

g) Reactions using Phenylsilveracetylide

Preparation of Phenylsilveracetylide

$$C_6H_5C{\equiv}CH + AgNO_3 = C_6H_5C{\equiv}CAg + HNO_3$$

Silver nitrate (40 g., 0.235 mole) was dissolved in a mixture of water (100 c.c.) and methanol (100 c.c.) in a 500 c.c. 3-necked flask fitted with, a stirrer (with a nitrogen inlet), a dropping funnel and a nitrogen outlet. Air was removed from the apparatus by passing a rapid stream of nitrogen through it for a few minutes. After this stage a minimum flow of nitrogen was passed through the apparatus. Sufficient concentrated ammonia (sp. g. 0.880) was then added to redissolve the precipitate of silver oxide formed. A solution of phenylacetylene (20 g., 0.196 mole) in methanol (20 c.c.) was added over 20 minutes with vigorous stirring. White solid was precipitated immediately. After stirring for another 30 minutes the solid was filtered, washed repeatedly with water and then in turn with methanol, acetone and finally ether. The solid was then dried, <u>in vacuo</u> (2 hours). The very pale yellow solid was then powdered, there being obtained phenylsilveracetylide (43.3 g., 106% yield). The high yield was probably due to the inclusion of silver nitrate (or ammonium nitrate) in the silveracetylide.

Reactions of Phenylsilveracetylide with Donor Compounds

As with the copperacetylides, the phenylsilveracetylide was treated with various electron-donor compounds to see with which co-ordination occurred most readily.

Phenylsilveracetylide dissolved in cold iso-propylamine, piperidine and pyridine yielding colourless or pale brown solutions. The silveracetylide was not soluble in cold or hot triethylamine. No reaction appeared to occur with a concentrated solution of dipyridyl in benzene, since the phenylsilveracetylide remained undissolved on standing overnight.

Addition of phenylsilveracetylide to diethyldithioethylene led to formation of a red solution, but large amounts of silveracetylide remained undissolved.

Reaction of triethylphosphine and triethylarsine with phenylsilveractylide resulted in immediate formation of almost colourless solutions.

Thus from the reactions studied it was concluded that co-ordination of phenylsilveracetylide occurred most readily with triethylphosphine, triethylarsine and nitrogen containing compounds such as *iso*-propylamine, piperidine and pyridine.

Reaction between Phenylsilveracetylide and Triethylphosphine

$$C_6H_5C{\equiv}CAg + (C_2H_5)_3P = C_6H_5C \equiv C\overset{-}{A}g \leftarrow \overset{+}{P}(C_2H_5)_3.$$

Phenylsilveracetylide (16 g., 0.077 mole) was stirred in a 250 c.c. 3-necked flask fitted with, a stirrer (with a nitrogen inlet), a dropping funnel and a nitrogen outlet. A solution of triethylphosphine (12 g., 15 c.c., 0.103 mole) in toluene (30 c.c.) was added over 15 minutes. After stirring for another 15 minutes a yellow solution was formed, with small amounts of grey solid and a white oily liquid. After this stage in the preparation the reaction material was handled in air, but keeping such exposure to a minimum. The grey solid was removed by filtration through hyflo super cel and addition of anhydrous magnesium sulphate, followed by filtration, removed the oily liquid, yielding a clear yellow solution. Addition of a large volume of n-hexane (ca. 200 c.c.) to the clear solution caused precipitation of pale pink needle-like crystals. On warming a clear yellow solution resulted, which, on cooling, deposited pale pink crystals. These were filtered off. Another crop of crystals was obtained by cooling the filtrate to ca. -80°C. and then refiltering. After pumping, in vacuo, pale pink crystals (14.5 g., 64% yield of co-ordination compound) remained. About half of the solid was then recrystallised from hot n-hexane, containing a little toluene, colourless crystals being obtained. Samples of this material were then analysed (Found: Ag, 30.68, 30.44; C, 46.88; H, 6.10. $C_{14}H_{20}AgP$ requires: Ag, 32.98; C, 51.39; H, 6.16%). Although the values obtained for silver and carbon were low they indicated that the compound, $\left[C_6H_5C{\equiv}CAg.P(C_2H_5)_3\right]_n$, had been formed.

Solubility tests carried out on samples of this solid showed that it was very soluble in acetone, benzene, toluene, ethylacetate, chloroform, methylethylketone and dioxan. When samples of the solid were warmed with alcohol a feathery white precipitate formed, which was insoluble in the solvents mentioned above, i.e., breakdown to phenylsilveracetylide. The solid, however, crystallised readily from hot methylcyclo-hexane.

When an attempt was made to recrystallise some of the material analysed previously from hot n-hexane, a small amount of grey insoluble solid was observed (silver). This suggested that the compound decomposed on standing. The solid was removed by filtration and the material was recrystallised and pumped dry as before. Samples of this material were then analysed for silver (Found: Ag, 32.28, 32.08. $C_{14}H_{20}AgP$ requires Ag, 32.98%). Another sample of material recrystallised from methyl-cyclo-hexane was analysed for carbon and hydrogen (Found: C, 49.39; H, 6.14. $C_{14}H_{20}AgP$ requires: C, 51.39; H, 6.16%). Although the carbon value was rather low, the melting point of the compound 77.5-78.5°C. (from n-hexane) was sharp, confirming formation of the compound,

$$\left[C_6H_5C\equiv CAg.P(C_2H_5)_3\right]_n.$$

A sample of the compound was found not to be particularly air-sensitive, thus allowing recrystallisation in air, but the colourless crystals turned pink rapidly in bright sunlight.

The degree of association of the compound, "n", was determined in freezing benzene and nitrobenzene.

2.212 g. of $C_6H_5C\equiv CAg.P(C_2H_5)_3$ were dissolved in benzene (20 c.c.) of density 0.877 g./c.c. The original volume of benzene in the apparatus was 16 c.c.

a) Total volume of $C_6H_5C\equiv CAg.P(C_2H_5)_3$ sol. added to above = 4c.
b) Total volume of $C_6H_5C\equiv CAg.P(C_2H_5)_3$ sol. added to above = 9cc
c) Total volume of $C_6H_5C\equiv CAg.P(C_2H_5)_3$ sol. added to above = 16c.c

a) Freezing point depression = 0.154°C. Mol. Wt. = 839.
b) Freezing point depression = 0.267°C. Mol. Wt. = 871.
c) Freezing point depression = 0.361°C. Mol. Wt. = 894.

Thus, from the results obtained, the degree of association of the compound, $C_6H_5C\equiv CAg.P(C_2H_5)_3$, in freezing benzene, "n" = 2.5_6, 2.6_6, 2.7_3, at 0.068, 0.122, 0.170M.

2.024 g. of $C_6H_5C\equiv CAg.P(C_2H_5)_3$ were dissolved in nitrobenzene (20 c.c.); the solution rapidly turned red-violet on standing although no solid was precipitated. The original volume of nitrobenzene in the apparatus was 12 c.c. The density of the nitrobenzene was 1.199 g./c.c.

d) Total volume of $C_6H_5C\equiv CAg.P(C_2H_5)_3$ sol. added to above = 4c.c
e) Total volume of $C_6H_5C\equiv CAg.P(C_2H_5)_3$ Sol. added to above = 9c.c
f) Total volume of $C_6H_5C\equiv CAg.P(C_2H_5)_3$ sol. added to above = 14c.c

d) Freezing point depression = 0.220°C. Mol. Wt. = 659.

e) Freezing point depression = 0.370°C. Mol. Wt. = 672.

f) Freezing point depression = 0.455°C. Mol. Wt. = 686.

From the results obtained the degree of association of the compound, $C_6H_5C\equiv CAg.P(C_2H_5)_3$, in freezing nitrobenzene, "n" = 2.0_2, 2.0_5, 2.1 at 0.078, 0.133, 0.167M.

Ebullioscopically in benzene the degree of association of the compound, "n" = 1.5_9 over the concentration range 0.016-0.100M, and in ether, "n" = ca. 1.3 (best slope of graph) at 0.017-0.160M. The results obtained from boiling ether, which were plotted graphically (page 95), were very scattered so that the value obtained was not very accurate. Ebullioscopic measurements in acetone were abandoned, since decomposition (precipitation of silver) was observed.

Reaction between Phenylsilveracetylide and Triethylarsine

$$C_6H_5C\equiv CAg + (C_2H_5)_3As = C_6H_5C\equiv\overset{-}{C}Ag-\overset{+}{As}(C_2H_5)_3$$

Phenylsilveracetylide (4 g., 0.019 mole) was placed in a double Schlenk tube, which was filled with nitrogen in the usual way. Benzene (15 c.c.) and triethylarsine (4.6 g., 4 c.c., 0.035 mole) were then added. After standing ca. 3 hours some solid still remained so the mixture was warmed to 60°C, when a cloudy yellow solution containing a small amount of oily liquid was produced. The solution was filtered into the other limb of the Schlenk tube, a yellow solution being obtained, which deposited a white solid when cooled. The liquid was removed from the solid by filtration and the solid was dissolved in a mixture of toluene containing triethylarsine (ca. 3:1 by volume). On cooling to ca. -80°C. white solid was precipitated, filtered and removed from the Schlenk tube and dried by pumping, in vacuo (2 hours). It was found that in the absence of excess triethylarsine addition of toluene to the solid led to formation of insoluble phenylsilveracetylide, indicating that the reaction,

$$C_6H_5C{\equiv}C\bar{A}g\text{-}\overset{+}{A}s(C_2H_5)_3 \rightleftharpoons C_6H_5C{\equiv}CAg + (C_2H_5)_3As,$$

was reversible. Samples of the white solid were then analysed (Found: C, 45.10; H, 5.49; Ag, 27.91, 27.90. $C_{14}H_{20}AgAs$ requires: C, 45.30; H, 5.43; Ag, 29.08%). A sample of the compound melted at 89°C. The formation of the compound phenylsilveracetylidetriethylarsine, $\left[C_6H_5C{\equiv}C\bar{A}g\text{-}\overset{+}{A}s(C_2H_5)_3\right]_n$, was confirmed.

As found with the triethylphosphine analog, the arsine compound was not particularly air-sensitive, but turned pink rapidly in bright sunlight.

Reaction between Phenylsilveracetylide and iso-Propylamine

$$C_6H_5C{\equiv}CAg + (CH_3)_2CHNH_2 = C_6H_5C{\equiv}C\bar{A}g\text{-}\overset{+}{N}H_2CH(CH_3)_2.$$

Initial experiments had shown that phenylsilveracetylide dissolved readily in iso-propylamine. A sample of phenylsilveracetylide (4 g., 0.019 mole) was therefore extracted with iso-propylamine (20 c.c.), under nitrogen. After 2 hours extraction was completed and a brown solution was formed. No solid was precipitated on cooling to room temperature therefore iso-propylamine was removed, using a water-pump vacuum, until the residual material was almost solid. Addition of benzene to a sample of the material resulted in formation of a white precipitate, which was insoluble in boiling benzene. However, when iso-propylamine was added a clear solution was obtained. This indicated that the co-ordination compound dissociated in solution, i.e.,

$$C_6H_5C{\equiv}C\overset{-}{A}g{-}\overset{+}{N}H_2CH(CH_3)_2 \rightleftharpoons C_6H_5C{\equiv}CAg + (CH_3)_2CHNH_2,$$

the dissociation being suppressed in the presence of excess iso-propylamine. The remaining solid was therefore dissolved in the minimum amount of iso-propylamine and the solution produced was cooled to ca. -80°C. White crystalline material was obtained. After filtration and drying by pumping, in vacuo (1 hour), samples were analysed (Found: Ag, 50.18, 50.46. C_8H_5Ag requires: Ag, 51.64. $C_{11}H_{14}AgN$ requires: Ag, 40.25%). The results showed that loss of iso-propylamine from the co-ordination compound occurred in a vacuum.

Another sample of phenylsilveracetylide (4 g., 0.019 mole) was extracted with iso-propylamine (30 c.c.), as before, and the brown solution was transferred to a double Schlenk tube.

About 15 c.c. of *iso*-propylamine were removed, using a water-pump vacuum, but no solid was precipitated after standing for 2 hours. Heating at this stage produced a feathery solid, which was not very soluble in *iso*-propylamine. This solid dissolved on cooling to *ca.* -40°C. and shaking. On warming up to room temperature again white needle-like crystals were formed, which did not redissolve on cooling to -80°C. These crystals were filtered in the Schlenk tube and dried at 400 m.m. in an atmosphere of *iso*-propylamine in order to suppress dissociation of the co-ordination compound (1½ hours). Samples were then weighed quickly and analysed (Found: Ag, 42.41, 43.51. C_8H_5Ag requires: Ag, 51.64. $C_{11}H_{14}AgN$ requires: Ag, 40.25%). As found previously, these values were high for the adduct showing that loss of *iso*-propylamine had occurred. Another sample of the crystalline adduct, which had remained overnight in contact with *iso*-propylamine, was filtered rapidly on a sintered plate and weighed in a sealed vessel. The sealed vessel was attached to a vacuum apparatus, evacuated, and volatile material was collected and measured as gas; the residual involatile solid was also weighed (0.4813 g. of adduct, pumped, *in vacuo*, evolved 40.4N c.c., 22.1% iso-propylamine. The involatile solid (phenylsilveracetylide) weighed 0.3683 g. or 76.5% of the sample. The 1:1 adduct requires: 22.1% *iso*-propylamine, 77.9% phenylsilveracetylide). The gas, which could not be identified satisfactorily by v.p. measurements as *iso*-propylamine was identified by its infra-red spectrum. The formation of the co-ordination compound, $\left[C_6H_5C{\equiv}\overset{-}{C}Ag\text{-}\overset{+}{N}H_2CH(CH_3)_2\right]_n$ was thus confirmed.

h) Reactions using Methylsilveracetylide

Preparation of Methylsilveracetylide

$$CH_3C\equiv CH + AgNO_3 = CH_3C\equiv CAg + HNO_3 .$$

Silver nitrate (40 g., 0.235 mole) was dissolved in a mixture of water (100 c.c.) and methanol (100 c.c.) in a 3-necked 500 c.c. flask fitted with, a dropping funnel, a stirrer with a nitrogen inlet and a nitrogen outlet, to which a cold finger, filled with solid carbon dioxide, was attached in order to prevent loss of methylacetylene. The flask was filled with nitrogen and concentrated ammonia was added until the initial precipitate of silver oxide was just redissolved A solution of methylacetylene (7.8 g., 0.195 mole) in methanol (30 c.c.), cooled to -40°C, was then added to the stirred ammoniacal silver nitrate solution, which was cooled to 0°C. (10 minutes). A white precipitate formed immediately. After stirring for 30 minutes water (200 c.c.) was added and the solid was filtered, washed well with water, and then in turn with acetone and ether. Methylsilveracetylide (32.4 g., 113% yield) was obtained as a white powder after drying by pumping, *in vacuo* (3 hours). The product turned brown in sunlight and was therefore stored under nitrogen and kept in the dark. The high yield was probably due to the inclusion of some silver nitrate in the precipitate.

The Behaviour of Methylsilveracetylide with Various Donor Molecules

Samples of methylsilveracetylide were treated with various electron-donor compounds, to see with which co-ordination most readily occurred.

The silveracetylide did not dissolve in triethylamine, pyridine, iso-propylamine or piperidine, either cold or hot. There was no apparent reaction between dipyridyl dissolved in benzene, and methylsilveracetylide.

Methylsilveracetylide did not dissolve in diethylthioethylen although the liquid turned black on warming.

Methylsilveracetylide dissolved readily in triethylphosphine but more slowly in triethylarsine, producing rather cloudy brownish solutions.

Reaction between Methylsilveracetylide and Triethylphosphine

$$CH_3C{\equiv}CAg + (C_2H_5)_3P = CH_3C{\equiv}C\bar{A}g{-}\overset{+}{P}(C_2H_5)_3.$$

Methylsilveracetylide (4 g., 0.027 mole) was suspended in benzene (25 c.c.) in a double Schlenk tube filled with nitrogen and triethylphosphine (4.8 g., 6 c.c., 0.041 mole) was added. After shaking for 30 minutes all the white solid had dissolved leaving a small amount of black residue. The solution was filtered into the other limb of the Schlenk tube and benzene was removed by pumping, in vacuo, a brown solid being left. Samples of this solid dissolved readily in benzene and toluene, but not n-hexane or methyl-cyclo-hexane. There was an indication that dissociation occurred, since on heating the toluene solutio a white precipitate (methylsilveracetylide) was formed. A mixture of toluene and n-hexane (1:1 by volume) was used to recrystallise the brown solid by cooling a saturated solution at room temperature to -80°C. A greyish solid was obtained. As the grey colour was thought to be due to finely divided silver, the solid was dissolved in a toluene/n-hexane mixture and filtered through hyflo super cel. The clear colourless filtrate was then returned to the double Schlenk tube, recrystallised as before, a white crystalline product being obtained. When the white solid was dried by pumping, in vacuo, a brown colour was developed, indicating that decomposition had occurred.

Another quantity of methylsilveracetylide (8 g., 0.054 mole) was therefore suspended in toluene (40 c.c.) in a flask, under nitrogen, and triethylphosphine (9.6 g., 12 c.c., 0.081 mole) was added. The resultant reaction material was then filtered quickly through hyflo super cel into a double Schlenk tube, filled with nitrogen, a clear solution being obtained. n-Hexane (20 c.c.) was added and the solution was cooled to -80°C., when white crystals were obtained. The solid was filtered in the Schlenk tube and then washed out on to a sintered plate and dried by suction (2-3 minutes), and sealed up under nitrogen. Samples were dried finally by pressing on a filter-paper and analysed (Found: C, 24.45; H, 6.67; Ag, 38.88, 39.46. $C_9H_{18}AgP$ requires: C, 40.78; H, 6.84; Ag, 40.70%). The material stored under nitrogen and out of sunlight turned brown after standing overnight and after a few days was a very dark grey in colour.

As methylsilveracetylidotriethylphosphine could not be prepared readily in a pure state, and was not very stable, further study of methylsilveracetylide was discontinued.

i) Reactions using p-Nitrophenylcopperacetylide

Preparation of p-Nitrophenylcopperacetylide

Since the previous work had shown that phenylcopperacetylide formed a much more stable phosphine compound than the alkylcopperacetylides, it was of interest to discover the effect of an electron attracting group in the aromatic nucleus on the stability of the co-ordination compounds, i.e., by the use of an acetylene such as p-nitrophenylacetylene.

$$p\text{-}NO_2C_6H_4C{\equiv}CH + Cu(NH_3)_2Cl = p\text{-}NO_2C_6H_4C{\equiv}CCu + NH_4Cl + NH_3.$$

Cuprous chloride (3 g., 0.030 mole) was placed in a 500 c.c. flask fitted with a dropping funnel, a stirrer with a nitrogen inlet, and a nitrogen outlet. The flask was filled with nitrogen in the usual way. Water (100 c.c.) and sufficient concentrated ammonia was added until a clear very pale blue solution resulted. p-Nitrophenylacetylene (3 g., 0.020 mole) dissolved in ethyleneglycol dimethylether (30 c.c.) was then slowly added with vigorous stirring (30 minutes). A brick-red precipitate formed immediately. After stirring for another 30 minutes the solid was filtered, washed well with water, followed by alcohol, acetone and ether, and air dried. p-Nitrophenylcopperacetylide (4 g., 0.019 mole) was obtained in 95% yield as a brick-red powder, which was stable to blows, but decomposed vigorously on heating in a bunsen flame.

Reaction of p-Nitrophenylcopperacetylide with Various Donor Compounds

Samples of p-nitrophenylcopperacetylide were treated with various electron donor compounds, in sealed flasks, in order to find with which co-ordination occurred most readily.

There was no apparent reaction between p-Nitrophenylcopperacetylide and triethylamine, pyridine, *iso*-propylamine or dipyridyl, dissolved in benzene. The pyridine solution darkened on standing but solid remained undissolved. Addition of diethyldithioethylene to p-nitrophenylcopperacetylide resulted in the slow formation of a pink colour in the liquid but there was no indication that the copperacetylide was dissolving.

The copperacetylide dissolved slowly in triethylarsine on standing overnight, but the reaction with triethylphosphine was much faster resulting in formation of a deep-red solution.

Reaction between p-Nitrophenylcopperacetylide and Triethylphosphi

$$p\text{-}NO_2C_6H_4C{\equiv}CCu + (C_2H_5)_3P = p\text{-}NO_2C_6H_4C{\equiv}C\overset{-}{Cu}\text{-}\overset{+}{P}(C_2H_5)_3.$$

p-Nitrophenylcopperacetylide (3.5 g., 0.017 mole) was placed in a double Schlenk tube, which was filled with nitrogen, and benzene (25 c.c.) was added. Triethylphosphine (4.8 g., 6 c.c., 0.040 mole) was added. After shaking the Schlenk tube for 1 hour a deep red solution containing a small amount of oily brown solid resulted. The benzene was removed in a water-pump vacuum and the solid remaining was shaken with n-hexane (25 c.c.), which was then filtered into the other limb of the Schlenk tube. On cooling the solution to -80°C. crystals were deposited, and the n-hexane was filtered back into the other limb of the Schlenk tubes, and removed by pumping, *in vacuo*. Very dark red, almost black, crystals (7.2 g.), which appeared dark green by reflected light, were obtained and stored under nitrogen. These melted at 57°C., a sample left overnight in air decomposing to leave a brick-red powder.

A sample was analysed for copper, by the volumetric method (Found: Cu, 14.86. $C_{14}H_{19}CuNO_2P$ requires: Cu, 19.38%). The crystalline material was therefore recrystallised twice from hot n-hexane, dried by pumping, *in vacuo*, and reanalysed (Found: Cu, 11.96, 11.89; C, 39.95; H, 7.10. $C_{14}H_{19}CuNO_2P$ requires: Cu, 19.38; C, 51.30; H, 5.84%). As the analysis did not fit the 1:1 adduct and the copper was very low, although somewhat uncertain, since the colour of the solutions analysed obscured the end-point of the titration with ethylendiamminetetra-acetic acid, the formation of a 1:2 adduct containing two moles of phosphine was considered. The adduct was therefore recrystallised once more from hot n-hexane, which contained some triethylphosphine (5% by volume) in order to suppress any dissociation of the adduct which might occur. After drying the material was again analysed, copper being determined gravimetrically as the thiocyanate (Found: Cu, 14.81, 14.59; C, 50.47; H, 7.59. $C_{20}H_{34}CuNO_2P_2$ requires: Cu, 14.25; C, 53.87; H, 7.69%). Although the carbon value was low the analysis suggested that reaction between p-nitrophenylcopperacetylide and triethylphosphine led to formation of a 1:2 adduct instead of the usual 1:1 adduct.

j) Determination of Copper

i) Gravimetric Determination as Cuprous Thiocyanate[93]

$$2CuCl_2 + 2NH_4CNS + SO_2 + 2H_2O = 2CuCNS + (NH_4)_2SO_4 + 4HCl.$$

About 0.1 g. of sample was weighed in a beaker (100-150 c.c. which was covered by a watch glass. Initial decomposition of the sample was carried out by the dropwise addition of 5N nitric acid (ca. 1 c.c.). When the reaction moderated concentrated nitric acid (ca. 7 c.c.) was added, and the contents of the beaker were boiled until a clear blue solution resulted (5-15 minutes). The solution was allowed to cool somewhat, concentrated hydrochloric acid (ca. 10 c.c.) was added, and the solution was reboiled until no more oxides of nitrogen were evolved. If, on cooling, solid was formed (this generally occurred with arylcopperacetylides, which formed nitrobenzoic acids), the solution was filtered and the solid on the filter paper was washed well with water. A clear solution then resulted. After dilution to about 150 c.c. a saturated solution of sulphur dioxide (20 c.c.) was added and the solution was heated on a hot-plate for 30 minutes. If the smell of sulphur dioxide persisted (indicating that reduction of copper to the cuprous state was completed) the solution was removed from the hot-plate, but if not more sulphur dioxide solution was added and the heating process was repeated until an excess of sulphur dioxide was present. The solution was neutralised by the addition of sodium hydroxide solution until a permanent precipitate started to form. At this point the solution was cleared by the addition of 8-10 drops of concentrated hydrochloric acid, and then, for every 50 mg. of copper present, 10 c.c. of 2% ammonium thiocyanate solution saturated with sulphur dioxide was added from a burette with constant stirring. After standing overnight, the precipitate of cuprous thiocyanate was collected in a previously weighed sintered glass crucible (grade 4). The precipitate was washed with 1% ammonium sulphate solution, 20% alcohol, and finally alcohol, and dried to constant weight in an oven at 110-115°C. The precipitate was weighed as cuprous thiocyanate.

ii) Volumetric Determination of Copper[94]

A suitable weight of sample (ca. 0.1-.3 g.), such that a subsequent titer of 10-20 c.c. of ca. 0.02M EDTA (ethylenediammine tetra-acetic acid) was expected, was weighed in a beaker (100-150 c.c.). The sample was destroyed with nitric acid, and filtered if necessary, as described previously. The resultant clear solution was then made weakly acid as described in i), the volume of solution being adjusted to about 40 c.c. To each 10 c.c. of solution 0.5-1 c.c of concentrated ammonia was added and two drops of indicator (Fast Sulphon Black F). A violet colour, masked somewhat by the blue colour of the cuprammonium ions, was produced. The solution was titrated with ca. 0.02M EDTA. to a pale blue to bright green end point.

65.45 g. of copper ≡ 1000 c.c. of 1.0M EDTA.

The strength of the EDTA solution was determined by titration using a standard solution of copper sulphate. As EDTA reacts slowly with glass the solution was stored in a polythene container.

It was found that some of the copperacetylide/phosphine compounds, which still possessed a phosphine-like smell after boiling with concentrated nitric acid, tended to produce green solutions that were sufficiently coloured enough to mask the colour change of the indicator. For such cases method i), although much slower, is to be recommended.

k) Determination of Silver

$$AgNO_3 + KBr = AgBr + KNO_3.$$

Silver was determined by potentiometric titration of silver ion with potassium bromide.

A suitable weight of sample (0.5-1.5 g.) was weighed in a beaker (400 c.c.), covered with a clock glass. Initial decomposition was carried out with 5N nitric acid (*ca.* 1 c.c.), and, when the reaction had moderated, concentrated nitric acid (*ca.* 7 c.c.) was added. The mixture was then boiled until a clear solution resulted. After cooling, the solution was diluted with water (50 c.c.), a few drops of litmus solution were added, and the solution was neutralised with ammonia. Addition of about 10 drops of concentrated nitric acid then rendered the solution acid. More water was added to yield a solution of about 200 c.c.

Determination of silver was carried out using the apparatus shown in the diagram (Fig. 12). The silver electrode was coated with silver bromide, deposited by electrolysing an acid solution of potassium bromide with the silver as the anode. The glass electrode was filled with 1N potassium chloride solution. When not in use the electrodes were held in beakers of water, the silver electrode being kept in the dark. The e.m.f. of the system was measured after each addition of about 0.2N potassium bromide solution from a

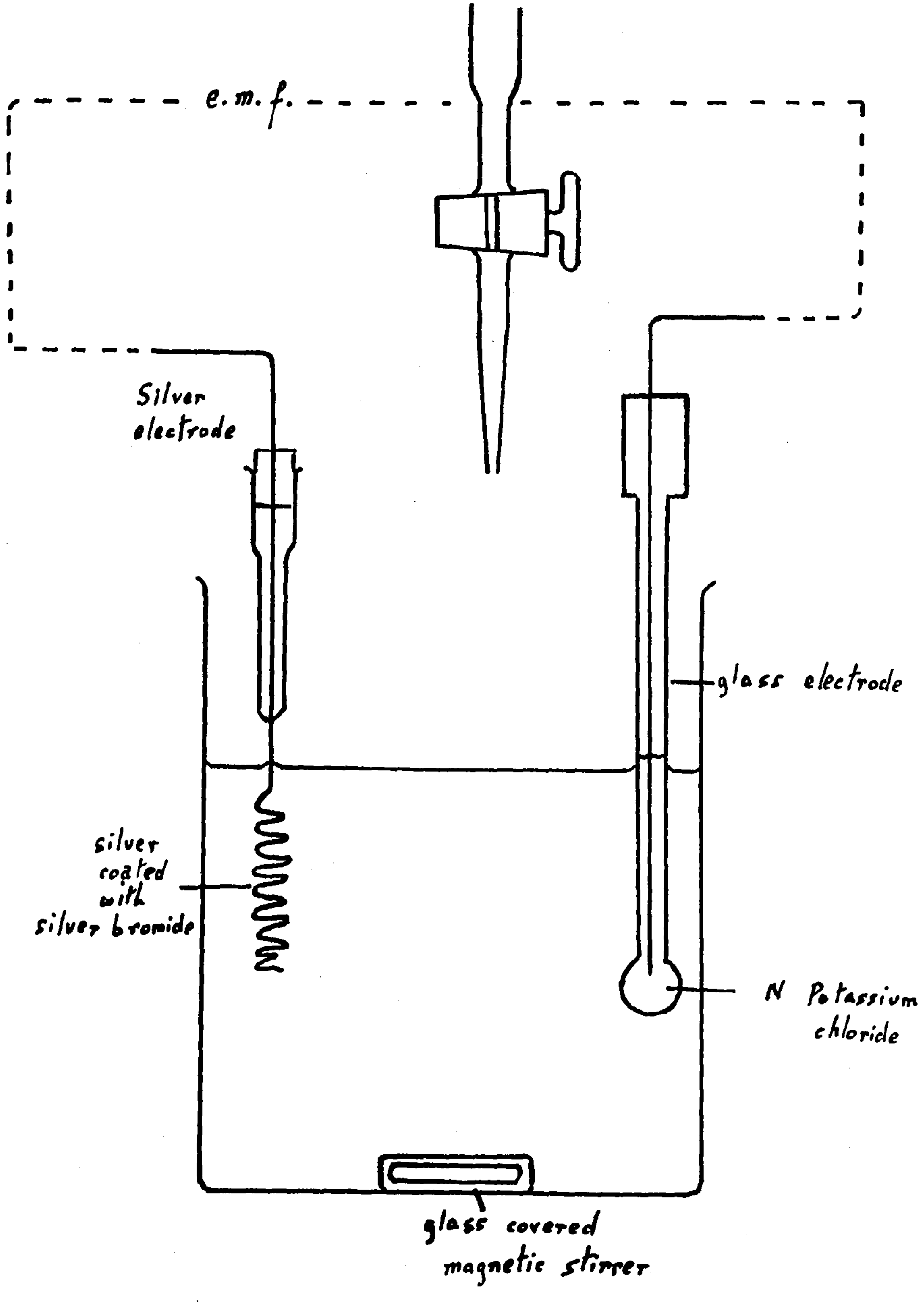

e.m.f.
Silver electrode
glass electrode
silver coated with silver bromide
N Potassium chloride
glass covered magnetic stirrer

Figure 12.

burette, time being allowed (10-15 seconds) for the mixture to be stirred thoroughly. When the end point of the titration was approached the increments of titer addition were decreased progressively to 0.05 c.c. It was found that near the end point, when coagulation of the silver bromide started to occur, the mixture had to stir for 2-3 minutes before the e.m.f. reading became steady. A graph of e.m.f. in millivolts against volume of potassium bromide solution was plotted. The point of inflection of the curve obtained was taken as the end point of the titration. The potassium bromide was standardised, by this method, with silver nitrate of known normality.

Organic solid was generally formed in the solutions prepared for analysis. It was found, however, that removal of the solid, by filtration, was unnecessary, since the end point of the titration was unchanged. Similarly the use of an acetone/water solvent, which dissolved the organic solid, did not affect the end point.

1) Molecular Weight Determinations

i) In Freezing Solvents

The apparatus used was set up as shown in the diagram (Fig. 14). When in use the apparatus was immersed in a 4l. beaker containing an ice/water mixture, which was stirred mechanically. Air was excluded from the apparatus, when air-sensitive compounds were determined, by means of a stream of nitrogen, which escaped from the top of the freezing point tube. The nitrogen was saturated with the solvent used in the determination by passage through two traps cooled to about the same temperature as the ice/water bath.

A known volume (usually 12 c.c.) of solvent was added to the apparatus, and its freezing point was determined with the Beckmann thermometer. The solvent was stirred gently until it was supercooled (ca. 0.02°C.), when brisk stirring sufficed to induce crystallisation.

The ice/water bath was maintained 1-3°C. below the freezing point of the solvent. A graph of temperature against time was plotted. Extrapolation of the straight line, which occurred after crystallisation, to the original curve yielded the correct freezing point. Various volumes of solution (a known weight of compound ca. 1 g. was dissolved in 20-25 c.c. of solvent, the density of the solvent assumed to be unchanged) were then added and their freezing points were determined similarly. Although air-sensi-

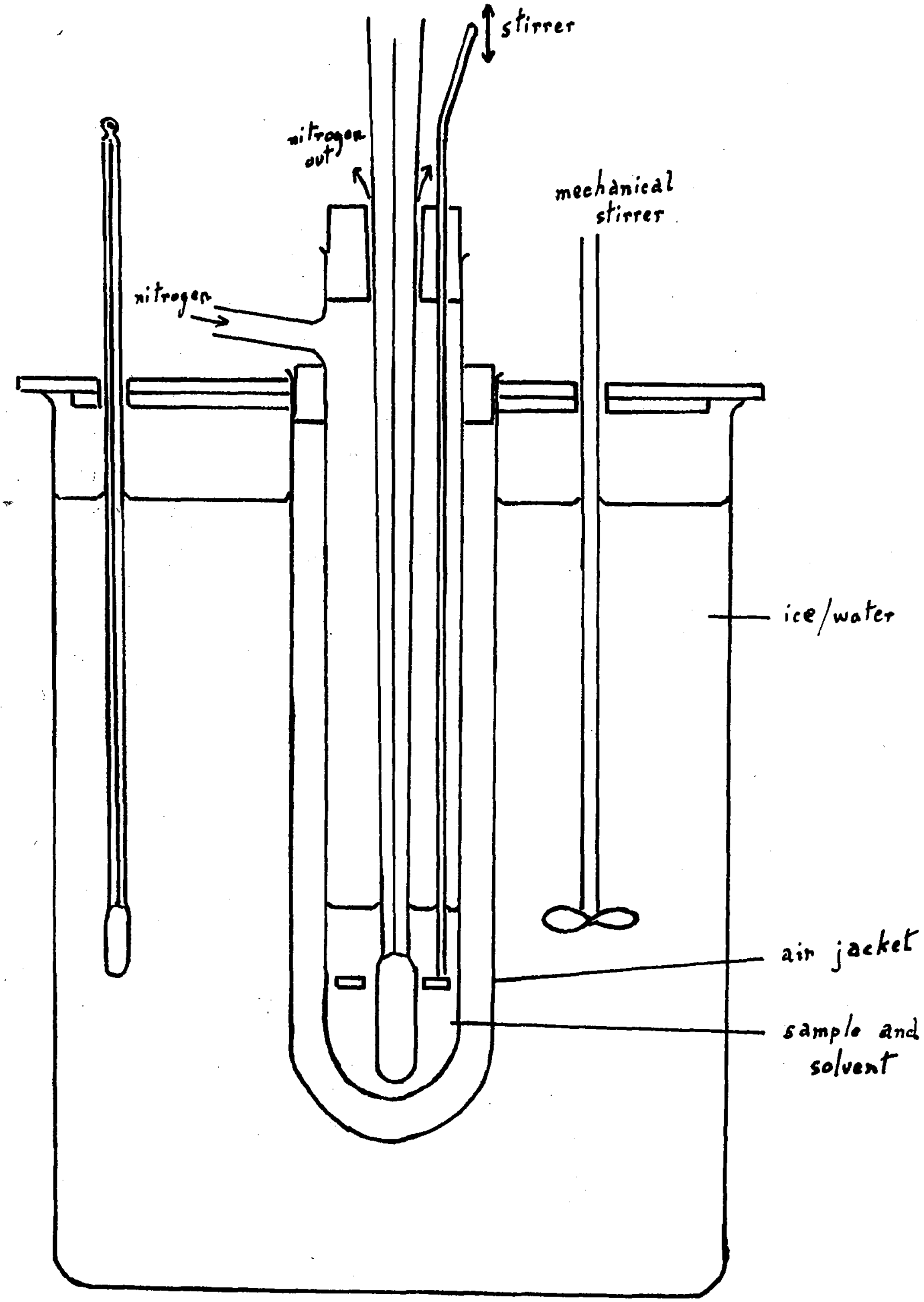

stirrer
nitrogen out
nitrogen
mechanical stirrer
ice/water
air jacket
sample and solvent

Figure 14.

tive solids were sometimes determined, the reaction with air in solutions was slow enough to permit addition from a burette or pipette. The solution was, however, kept in a flask under nitrogen as much as possible. Thus, from the expression[95]:

$M = K \frac{w}{dW}$, where "w" is the weight of solute dissolved in "W"g. of solvent, "d" the depression of the freezing point and "K" the freezing point constant, a series of molecular weights at various concentrations was obtained.

The following example illustrates the method.

A sample of t-butylcopperacetylide (1.5795 g.) was weighed in a conical flask (50 c.c.). A known volume of benzene (18 c.c.) of known density (0.877 g./c.c.) was added yielding a deep red solution. Another known volume of benzene (12 c.c.) was added to the apparatus and its melting point was determined using a Beckmann thermometer (4.298° in arbitrary Centigrade units). Known volumes of the t-butylcopperacetylide solution (4, 8, 12 and 14.5 c.c. total volumes added respectively) were added to the benzene in the apparatus, the freezing point of the solution being measured after each addition of t-butylcopperacetylide solution. A series of freezing points for solutions containing increasing concentrations of t-butylcopperacetylide was obtained (4.187°, 4.122°, 4.080° and 4.078° for 4,8,12 and 14.5 c.c. of t-butylcopperacetylide added to the 12 c.c. of benzene in the apparatus). Thus, if the density of the t-butylcopperacetylide solution is assumed to be the same as the benzene:

a) Wt. of t-$C_4H_9C\equiv CCu$ sol. added to 12 c.c. of benzene = .351 g., Total vol. = 16 c.c.

b) Wt. of t-$C_4H_9C\equiv CCu$ sol. added to 12 c.c. of benzene = .702 g., Total vol. = 20 c.c.

c) Wt. of t-$C_4H_9C\equiv CCu$ sol. added to 12 c.c. of benzene = 1.053 g., Total vol. = 24 c.c.

d) Wt. of t-$C_4H_9C\equiv CCu$ sol. added to 12 c.c. of benzene = 1.273 g., Total vol. = 26.5 c.c.

a) Freezing point depression of above solutions = 0.111°C.

b) Freezing point depression of above solutions = 0.176°C.

c) Freezing point depression of above solutions = 0.218°C.

d) Freezing point depression of above solutions = 0.220°C.

Using the expression,

$M = K \frac{w}{Wd}$, where the letters denote the quantities described previously, then:

a) $M = 5{,}120 \times 0.351 \times \frac{1}{16 \times .877 \times .111} = \underline{\underline{1{,}154}}$

b) $M = 5{,}120 \times 0.702 \times \frac{1}{20 \times .877 \times .176} = \underline{\underline{1{,}165}}$

c) $M = 5{,}120 \times 1.053 \times \frac{1}{24 \times .877 \times ,218} = \underline{\underline{1{,}176}}$

d) $M = 5{,}120 \times 1.273 \times \frac{1}{26.5 \times .877 \times .220} = \underline{\underline{1{,}275}}$

ii) <u>In Boiling Solvents</u>

The ebullioscopic molecular weight measurements were carried out in a Swietoslawsky type ebulliometer. The

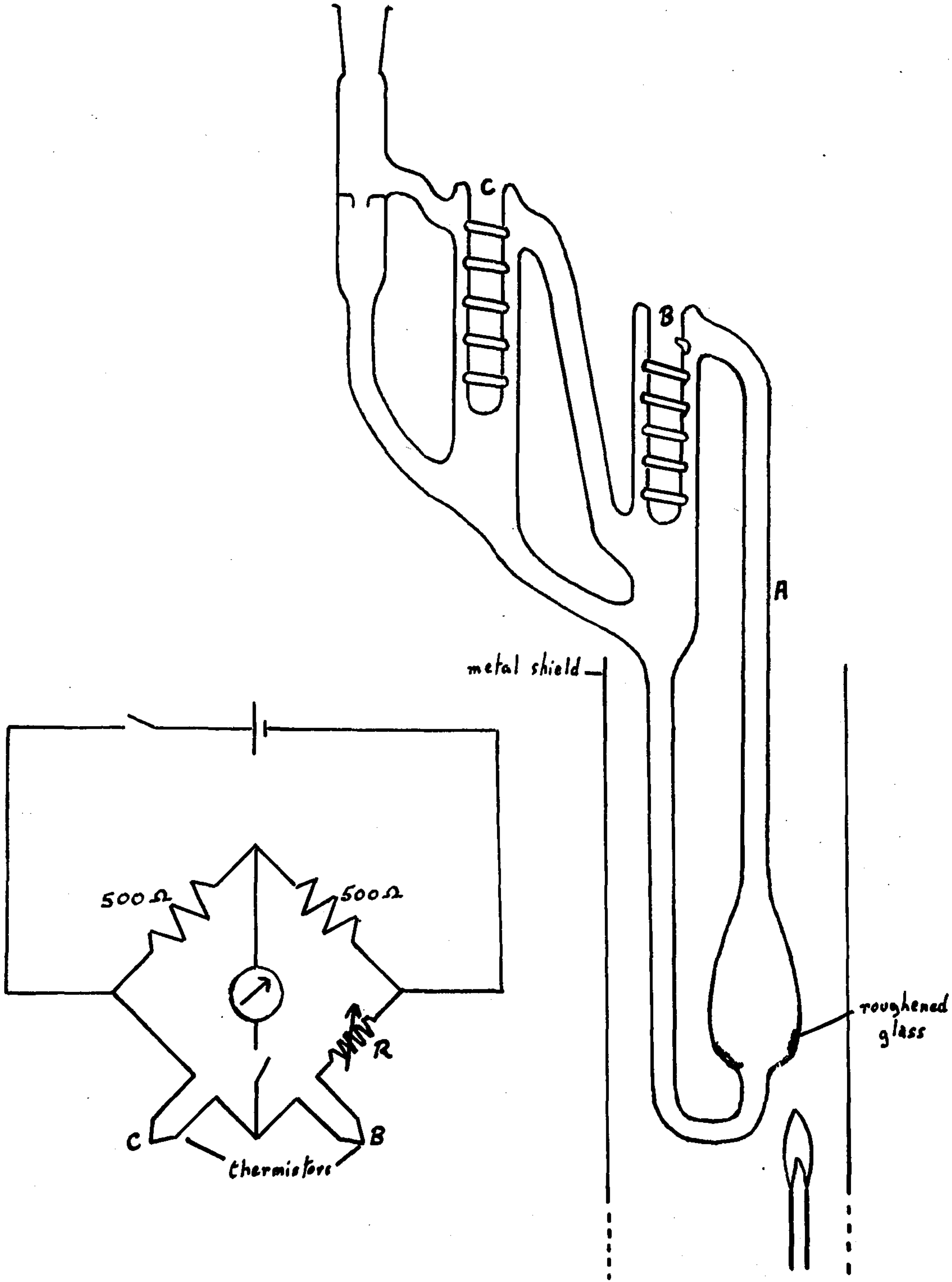

C
B
A
metal shield
roughened glass
500 Ω
500 Ω
R
C
B
thermistors

Figure 15.

apparatus and circuit are shown in the diagram (Fig. 15).

The boiler of the apparatus has an area of roughened glass, which facilitates boiling of the solvent. Two matched thermistors are fitted into the thermometer wells, good thermal contact between vapour and liquid being maintained by a pool of heavy white oil in each well. The boiler and syphon tube were protected from draughts by a metal tube and the apparatus was well lagged with cotton wool. Two condensers, connected in series, were fitted to the apparatus.

Aknown volume of solvent (25-30 c.c.) was boiled steadily with a micro-burner. The boiling solvent (or solution) syphoned up the tube A and heated the thermistor B. The pure solvent vapour distils further, heats thermistor C and finally refluxes at a constant height in the lower condenser. The two thermistors B and C are therefore at the temperature of the solvent (or solution) and solvent vapour, and the difference in their resistances is proportional to the elevation of the boiling point (of the solution).

After thermal equilibrium is attained (<u>ca</u>. 45 minutes) the resistance R, in the Wheatstone bridge, is adjusted until the galvanometer deflection is zero. This balances slight temperature differences between liquid solvent and its vapour; the resistance, R_o, was noted. A known weight of solute was introduced from the top of the lower condenser, so that none adhered to the ground glass joint. The upper condenser was replaced and the water was drained from the lower condenser. Solvent vapour then climbed up the lower condenser, dissolving the adhering solute and washing it into the apparatus.

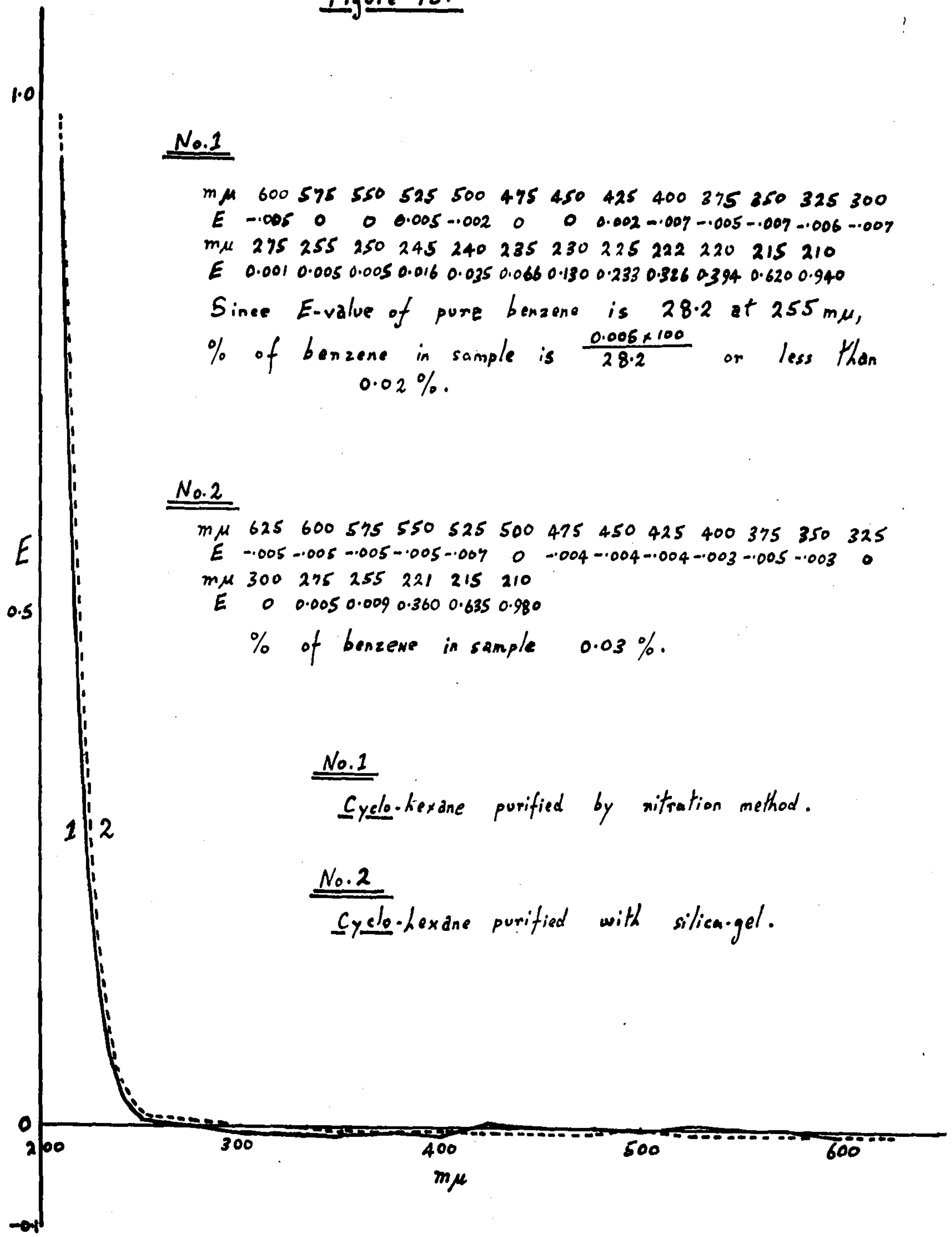
The lower condenser was then refilled with water and the apparatus was left to settle down to thermal equilibrium (*ca.* 10 minutes). The bridge was now out of balance, due to B being at a higher temperature and R was increased to give zero deflection of the galvanometer, the reading R_1 being obtained.

The increase in resistance (R_1-R_o) is proportional to the elevation of the boiling point, which is also proportional to the number of moles of solute. This procedure was repeated giving a series of resistance increments (R_1-R_o), (R_2-R_o), *etc.*, corresponding to a series of total weights of solute.

The apparatus was calibrated with a particular solvent using a solute of known molecular weight (diphenyl or benzophenone). A graph of Δ R in ohms against total number of moles of solute added was then drawn. The graphs obtained are linear in the concentration range used (0-3 m. moles of solute in 25 c.c. of solvent) and pass through the origin. Thus, with a solute of unknown molecular weight, the number of moles corresponding to the resistance increment is read off the calibration graph. This value divided into the weight of solute then yields the molecular weight.

It was found that with certain solvents (such as benzene, methylene chloride and tetrahydrofuran) frothing occurred. This brought solution into contact with the vapour temperature well, thus rendering results invalid, since the thermistor C no longer measured the temperature of the pure vapour. However, this difficulty was overcome by dispensing with the thermistors and placing a Beckmann thermometer in well B. The reading of the thermometer was then noted for the boiling solvent, T_o, and with various increments of solute, T_1, T_2...., yielding a series of elevations in boiling point, (T_1-T_o), (T_2-T_o), ..., for various weights of solute. A calibration graph was constructed using a compound of known molecular weight, plotting, in this case, the elevation of boiling point instead of increase in resistance against moles of solute. A similar linear graph resulted, since each elevation of the boiling point (T_1-T_o) was proportional to the number of moles of solute. Molecular weights were calculated as before.

Figure 13.



No.1

mμ	600	575	550	525	500	475	450	425	400	375	350	325	300
E	-·005	0	0	0·005	-·002	0	0	0·002	-·007	-·005	-·007	-·006	-·007

mμ	275	255	250	245	240	235	230	225	222	220	215	210
E	0·001	0·005	0·005	0·016	0·035	0·066	0·130	0·233	0·326	0·394	0·620	0·940

Since E-value of pure benzene is 28·2 at 255 mμ, % of benzene in sample is $\frac{0{\cdot}006 \times 100}{28{\cdot}2}$ or less than 0·02 %.

No.2

mμ	625	600	575	550	525	500	475	450	425	400	375	350	325	
E	-·005	-·005	-·005	-·005	-·007	0	-·004	-·004	-·004	-·003	-·005	-·003	0	

mμ	300	275	255	221	215	210
E	0	0·005	0·009	0·360	0·635	0·980

% of benzene in sample 0·03 %.

No.1

Cyclo-hexane purified by nitration method.

No.2

Cyclo-hexane purified with silica-gel.

m) Purification of Cyclo-hexane

Cyclo-hexane was purified, as described below, in order to remove traces of benzene, which would have absorbed light in the region where some of the adsorption experiments were carried out.

i) Cyclo-hexane (1.5 l.) was shaken mechanically with a nitrating mixture (400 c.c. concentrated sulphuric acid; 200 c.c. concentrated nitric acid) over 6 hours.[96] The cyclo-hexane was then washed with water and potassium hydroxide solution, until the aqueous phase was colourless. Finally the cyclo-hexane was washed with water (3 times) and then dried over magnesium sulphate. The dried product was distilled through a helices column (60 cms.). The initial fraction was yellow and nitrogen oxide fumes were observed in the apparatus, but these disappeared on continued distillation, a clear colourless distillate being obtained, b.pt. 79.5°C. The initial yellow distillate (250 c.c.) and undistilled liquid (250 c.c.) were rejected. The purity of the middle fraction (cal. 1.) was ascertained by its light adsorption down to 200 mμ, a comparison cell of distilled water being used (Fig. 13).

ii) Cyclo-hexane was also purified[96] by passage through a silica-gel column (about 400 g. of silica-gel per 1-1.5 l. of cyclo-hexane). The product was only slightly less pure than that prepared in i), and the method was much simpler.

3. Discussion of Results

a) Alkylcopperacetylide Complexes

Reactions studied with methylcopper- and *t*-butylcopperacetylides showed that the co-ordinating strength of Group V donor atoms is in the order $N \ll P > As$. There were indications that reaction occurred with triethylarsine and *t*-butylcopperacetylide but co-ordination must have been very weak, since it could not be detected by ultra-violet adsorption spectroscopy (page 68). Reactions with sulphur compounds also showed that little or no co-ordination occurred. On the other hand the reaction between methylcopperacetylide and triethylphosphine resulted in formation of a new co-ordination compound, methylcopperacetylide triethylphosphine. Similarly the reaction between *t*-butylcopperacetylide and triethylphosphine yielded a product, which could not be purified satisfactorily, but which probably contained the desired co-ordination compound. Ultra-violet adsorption measurements on various mixtures of *t*-butylcopperacetylide and triethylphosphine in *cyclo*-hexane supported this conclusion. As the mixtures containing over one molar equivalent of triethylphosphine showed decreases in adsorption from that of an equimolar mixture of *t*-butylcopperacetylide and triethylphosphine, it was concluded that in solution the following equilibrium was set up:

$$\underline{t}\text{-}C_4H_9C\equiv CCu + (C_2H_5)_3P \rightleftharpoons \underline{t}\text{-}C_4H_9C\equiv C\overset{-}{C}u\text{-}\overset{+}{P}(C_2H_5)_3.$$

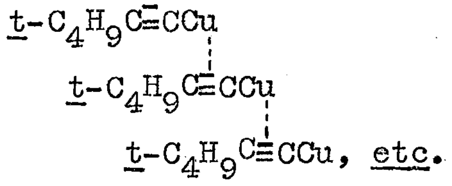
The reaction of methylcopperacetylidetriethylphosphine in solution confirmed this, since, on addition to benzene, the yellow insoluble methylcopperacetylide was precipitated. Addition of a small amount of triethylphosphine to the solution then resulted in formation of a clear colourless solution. Evidently in solution, at least, an excess of triethylphosphine is necessary to prevent dissociation of the alkylcopperacetylide complex by driving the equilibrium,

$$R\text{-}C{\equiv}CCu\text{-}P(C_2H_5)_3 \rightleftharpoons R\text{-}C{\equiv}CCu + P(C_2H_5)_3,$$

to the left. This effect was not noticeable with _t_-butylcopperacetylide, since the copperacetylide is soluble in organic solvents such as benzene and _cyclo_-hexane.

Since _t_-butylcopperacetylide is soluble in organic solvents it was possible to carry out molecular weight determinations in freezing benzene. The results confirmed earlier work[91] and indicated that the copperacetylide was highly associated, "n" being about 8. Similarly it was possible to carry out molecular weight measurements of methylcopperacetylidetriethylphosphine in freezing benzene by making use of the fact that a small excess of triethylphosphine prevented precipitation of methylcopperacetylide. These results showed that the complex was also highly associated, "n" being about 9.

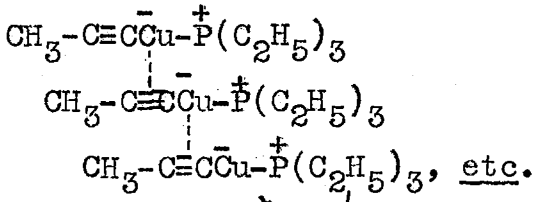
The polymerisation of _t_-butylcopperacetylide has been attributed to bonding between the copper and the acetylene group:[91]



$$\begin{array}{l} t\text{-}C_4H_9C\equiv CCu \\ \quad t\text{-}C_4H_9C\equiv CCu \\ \qquad t\text{-}C_4H_9C\equiv CCu,\ \text{etc.} \end{array}$$

..... partial or weak bonding

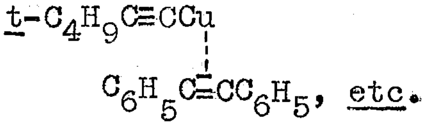
Such bonding between copper and unsaturated hydrocarbons is known to occur with cuprous halides.[13-16] It has also been shown that the more alkyl groups are attached to the carbons of the unsaturated linkage the weaker is the co-ordination compound formed. Thus it is reasonable to suppose that the polymerisation of the phosphine complexes arises from a similar phenomenon, *e.g.*,



$$\begin{array}{l} CH_3\text{-}C\equiv C\overset{-}{Cu}\text{-}\overset{+}{P}(C_2H_5)_3 \\ \quad CH_3\text{-}C\equiv C\overset{-}{Cu}\text{-}\overset{+}{P}(C_2H_5)_3 \\ \qquad CH_3\text{-}C\equiv C\overset{-}{Cu}\text{-}\overset{+}{P}(C_2H_5)_3,\ \text{etc.} \end{array}$$

The increased ~~electro-negativity of~~ negative charge on the copper atom, due to co-ordination, in this case would be expected to weaken the bond between the copper and acetylene group. Further, the *t*-butyl group, which is a much stronger electron repelling group than the methyl, would be expected to yield a weaker co-ordination complex, and less highly associated copperacetylide, because it would tend to make the copper relatively more electronegative than the methyl group. Thus methylcopperacetylide would be expected to be more associated than *t*-butylcopperacetylide, which is supported by the fact that t-butylcopperacetylide is soluble in organic solvents but not methylcopperacetylide. Formation of methylcopperacetylidetriethylphosphine yields a complex soluble in organic solvents, probably by partial depolymerisatio due to reduction of the metal-acetylene group interaction, although the co-ordination compound is still highly associated. The complex t-butylcopperacetylidetriethylphosphine would be expected to be less associated than t-butylcopperacetylide and methylcopperacetylide.

The difficulty in preparing a pure t-butylcopperacetylide triethylphosphine complex suggests that it is more highly dissociated in solution than the analogous methyl compound. The resul of the adsorption experiments between t-butylcopperacetylide and diphenylacetylene (page 63) are also relevant to this discussion, since it was found that the extinctions of solutions of t-butylcopperacetylide in *cyclo*-hexane gradually decreased as more diphenylacetylene was added. Such a phenomenon might be attributable to weak co-ordination of the acetylene group of the diacetylene with some of the copper atoms from the acetylide, *i.e.*,



$$\begin{array}{l} t\text{-}C_4H_9C{\equiv}CCu \\ \qquad\qquad\quad \vdots \\ \qquad\qquad C_6H_5C{\equiv}CC_6H_5, \end{array}$$ *etc.*

The alkylcopperacetylides are generally stable in air, but it was found that methylcopperacetylidetriethylphosphine rapidly turned green-blue after standing in air for a few minutes. Thus, if the stability of the alkylcopperacetylides is dependent on the bonding between the copper and acetylene group, any weakening of this bond, as in co-ordination, would be expected to yield a less stable product. The oxidation of *t*-butylcopperacetylide by alkaline potassium ferricyanide can be expressed by the equation:[91]

$$2\underline{t}\text{-}C_4H_9C{\equiv}CCu + H_2O + 3\,[O] \longrightarrow (\underline{t}\text{-}C_4H_9CH_2COO)_2Cu + CuO$$

This reaction only occurred slowly at room temperature.

In the co-ordination compounds, however, there is the possibility that oxidation occurs in moist air in a manner similar to that of the oxidation of copper acetylides in ammoniacal solution, by air or alkaline ferricyanide, when the diacetylene results. Thus in the case of methylcopperacetyli triethylphosphine a reaction of the type,

$$CH_3C{\equiv}C\overset{-}{C}u\text{-}\overset{+}{P}(C_2H_5)_3 \xrightarrow[H_2O]{[O]} CH_3C{\equiv}C\text{-}C{\equiv}CCH_3 + Cu(OH)_2 + (C_2H_5)_3PO,$$

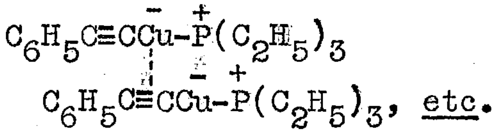
probably occurs, the green-blue colour indicative of formation of a cupric salt being observed, the triethylphosphine functioning in a manner similar to that of the ammonia mentioned above.

b) Aromatic copperacetylide Complexes

The same trend of stability of co-ordination complexes was shown by phenylcopper- and *p*-nitrophenylcopper- acetylides with nitrogen, phosphorus and arsenic as with the alkylcopperacetylides.

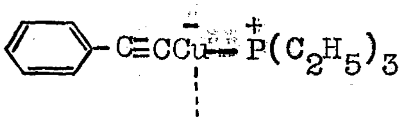
The reactions with triethylphosphine occurred much more readily than those with triethylarsine, and, in the case of phenylcopperacetylide, even with o-phenylene-bis-dimethylarsine. There was, however, no opportunity to follow these observations any further. It was found that phenylcopperacetylide dissolved in piperidine and iso-propylamine, but not p-nitro-phenylcopperacetylide, although no products were isolated. A weak co-ordination compound, $C_6H_5C{\equiv}CCu.NH_3$, has been reported, which rapidly looses its ammonia at room temperature and reverts back to the yellow phenylcopperacetylide.[1] This compound resulted when liquid ammonia was condensed on to phenylcopperacetylide, a colourless solid being obtained.

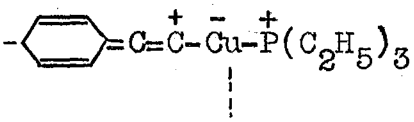
Research on the aromatic-copperacetylides was thus practically confined to the triethylphosphine complexes, which were the most readily accessible. There were some important differences in properties between the aromatic and alkyl complexes. The compound phenylcopperacetylidetriethylphosphine, which was isolated as yellow needles (the corresponding methyl compound was colourless), was unlike the analogous alkyl complexes in that it was reasonably stable in air. A sample only turned green after exposure to air for about two days. The compound did not dissociate in solution like methylcopperacetylidetriethylphosphine, even in boiling benzene or cyclo-hexane, from which it was possible to recrystallise. Molecular weight determinations in benzene and nitrobenzene indicated that the association of phenylcopperacetylidetriethylphosphine was much less than that found for the analogous methyl compound, being about 3 to 3.5. Although the association is similar to that found for the cuprous iodide trialkylphosphine complexes,[45,4] the structure,[45] which was discussed previously (page 10), is unlikely to be the same, since it would involve large straining of the acetylene group. The product is probably associated in the manner postulated for the alkyl compounds:



$$\begin{array}{l} C_6H_5C\equiv C\overset{-}{Cu}-\overset{+}{P}(C_2H_5)_3 \\ \qquad C_6H_5C\equiv C\overset{-}{Cu}-\overset{+}{P}(C_2H_5)_3,\ \underline{\text{etc}}. \end{array}$$

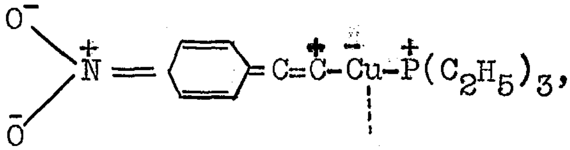
In this case, however, it is possible for stabilisation of the product to occur by reduction of the formal charge on the copper via induction and formation of a resonance hybrid between the two forms:



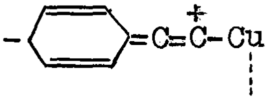


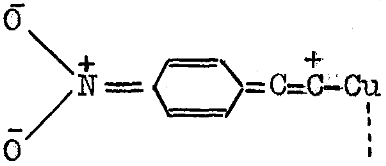
Such a contribution to the bonding might also be expected to lead to adsorption of light in the visible region, as found in the phenyl compound.

In the case of the p-nitrophenylcopperacetylide co-ordination with triethylphosphine caused a colour change from a brick-red to deep red, almost black colour. Such a deepening of colour would be expected by formation of a longer cönjugated system, i.e., by an increased contribution in the conanical form,

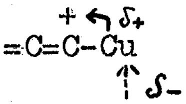


to the final resonance hybrid. It is interesting to note that a deepening of colour from yellow to red occurs when a nitro group is added to phenylcopperacetylide. Again this is consistent with formation of a longer conjugated system, e.g.,





In the copperacetylides the weak bond between the copper and the acetylene group would reduce the induced positive charge on the copper atoms, e.g.,



$$=C=\overset{+}{C}\overset{\curvearrowleft}{-}\underset{\uparrow\,\delta-}{\overset{\delta+}{Cu}}$$

movement of electrons →

The phosphine in the co-ordination compounds, however would be expected to be a much greater electron donor than the acetylene group and thus be expected to be much more strongly bonded. This would increase the electronegativity of the copper and thus tend to reduce the partial bonding between the copper and acetylene groups. However, since it was not possible to determine molecular weights, due to the insolubility of the copperacetylides, this effect could not be demonstrated.

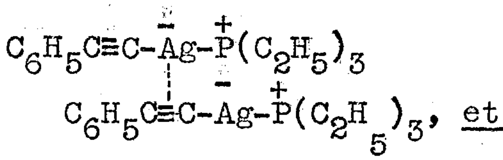
The *p*-nitrophenylcopperacetylide differed from the other acetylides in that it appeared that co-ordination with up to two molecules of triethylphosphine could occur. It was not, however, possible to carry out further research on this reaction.

c) Co-ordination Compounds of Phenylsilveracetylide

The donor strength of the Group V elements with phenylsilveracetylide was similar to that found with the copperacetylide, *i.e.*, $N \ll P > As$, the reaction with triethylarsine being almost as fast as that with triethylphosphi
This appears to be a case in which co-ordination with arsenic is much stronger than that found with both aryl- and alkyl-copperacetylides. The reactions of phenylsilveracetylide with *iso*-propylamine, piperidine and pyridine were also relatively fast, but there appeared to be no reaction with the sulphur-containing compound diethyldithioethylene (2,5-dithiohexane).

Phenylsilveracetylidetriethylphosphine was isolated as a colourless crystalline solid, which was not apparently oxygen sensitive, although a pink colour was developed in strong sunlight. On long standing some breakdown to silver was observed. This complex, like the analogous copper compound, did not dissociate in solution and could be recrystallised from boiling solvents such as *n*-hexane or methyl-*cyclo*-hexane.

Molecular weight determinations showed that the association (n) varied with the polarity and the temperature of the solvent, e.g., 'n' was ca. 2.7 in freezing benzene, ca. 2.1 in freezing nitrobenzene, 1.6 in boiling benzene and approximately 1.3 in boiling ether. The degree of association is less than that found for the analogous copper complex in freezing benzene. Variations in the degree of association with the polarity and temperature of the solvents is in accordance with the formation of weak bonds between the silver and acetylene group, i.e., association decreases with increasing polarity and temperature of the solvent. The structure of the complex is probably similar to that postulated for the copper compounds,



$$\begin{array}{l} C_6H_5C{\equiv}C\text{-}\overset{-}{Ag}\text{-}\overset{+}{P}(C_2H_5)_3 \\ \qquad C_6H_5C{\equiv}C\text{-}\overset{-}{Ag}\text{-}\overset{+}{P}(C_2H_5)_3, \end{array}$$

etc.

the bonding between the silver and acetylene group evidently being weaker in the silver compounds. Again there is the possibility of stabilisation of the compound by formation of a resonance hybrid as discussed earlier.

Although no co-ordination complex of phenylcopperacetylide with triethylarsine was isolated, the analogous phenylsilveracetylide complex was readily prepared. This complex was less stable than the triethylphosphine compound, since it dissociated in solution with precipitation of phenylsilveracetylide:

$$C_6H_5C{\equiv}\overset{-}{C}Ag\text{-}\overset{+}{A}s(C_2H_5)_3 \rightleftharpoons C_6H_5C{\equiv}CAg + (C_2H_5)_3As.$$

The complex was stabilised in solution by the presence of excess triethylarsine, this effect being similar to that which was observed with methylcopperacetylidetriethylphosphine.

The co-ordination complex formed by reaction between phenylsilveracetylide and iso-propylamine was only stable in the presence of excess *iso*-propylamine. *iso*-Propylamine was lost rapidly from the complex, *in vacuo*, or on standing in air or nitrogen.

Thus it appears that phenylsilveracetylide co-ordinates more readily with nitrogen, phosphorus and arsenic than the arylcopperacetylides, the relative donor strengths of the elements being the same in each case.

d) Co-ordination Compounds of Methylsilveracetylide

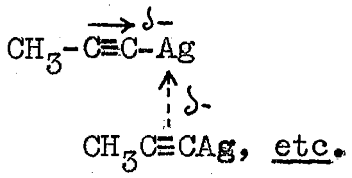
The alkylsilveracetylide co-ordination compounds were expected to be less stable than the aromatic ones by analogy with the copperacetylides. Thus it was found that methylsilveracetylide did not react with *iso*-propylamine, piperidine or dipyridyl dissolved in benzene and the reaction with triethylarsine was noticeably slower than that with triethylphosphine.

The reaction between methylsilveracetylide and triethylphosphine yielded a colourless, crystalline adduct, which turned brown rapidly, *in vacuo*, or under nitrogen and could not be purified satisfactorily. Even methylsilveracetylide was appreciably less stable than the alkylcopperacetylides, since it turned brown rapidly on standing under nitrogen, even in the dark.

The instability of the methylsilveracetylide complexes can be explained in terms of the electron repelling effect of the methyl group, which opposes the electron acceptance of the silver with donor elements, by increasing its electro-negativity,

$$CH_3\text{-}\overset{\xrightarrow{\delta-}}{C\equiv C}\text{-}\overset{-}{Ag}\text{-}\overset{+}{P}(C_2H_5),$$

and even co-ordination of the silver with the acetylene group:



$$\begin{array}{l} CH_3\text{-}\overset{\longrightarrow\delta-}{C\equiv C}\text{-}Ag \\ \qquad\quad \uparrow \delta- \\ \qquad CH_3C\equiv CAg,\ \underline{etc}. \end{array}$$

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