Organic phosphonium salts

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ORGANIC PHOSPHONIUM SALTS

by

J.M.F. Braddock

A thesis submitted for the degree of
Master of Science in the University of Durham.

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ACKNOWLEDGEMENTS

The author thanks Professor G.E. Coates for his supervision and advice given throughout this work. The helpful assistance of the teaching and laboratory staff is gratefully acknowledged.

MEMORANDUM

The work described in this thesis was carried out in the Durham Colleges of the University of Durham between September 1958 and August 1960. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

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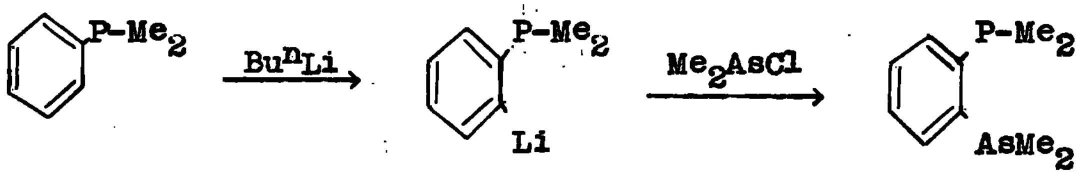
INTRODUCTION

In 1958 J.G. Livingstone, in this department, attempted to prepare o-dimethylarsinophenyldimethylphosphine by the metallation of phenyldimethylphosphine followed by reaction with cacodyl chloride.



The metallation was not successful and white crystals of dimethylarsinophenyldimethylphosphonium chloride were isolated. It was shown that the reaction which had taken place was:-

$$\mathrm{PhPMe_2 + Me_2AsCl \longrightarrow Me_2As{-}\overset{+}{P}{-}PhMe_2\quad Cl^-}$$

A few analogous phosphonium salts were prepared and the work was reported by G.E. Coates and J.G. Livingstone in Chemistry and Industry, 1958, 1366.

The earliest report of the preparation of organophosphonium salts e.g. $Me_4{-}P^+\ I^-$ was by Cahours and Hofmann in Ann., 1857, 104, 1. Since then the chemistry of the salts has been extensively studied and a comprehensive summary of them is given by Kosolapoff in in his book Organo-phosphorus Compounds, Wiley 1950. The salts prepared by Livingstone were the first to contain a Group V B element, other than phosphorus itself, bonded to the phosphorus atom. Sisler et al.[18] have studied the properties of some analogous salts prepared by the reaction of chloramine with tertiary phosphines.

$$R_3P + NH_2Cl \longrightarrow H_2N\text{-}P^+R_3 \quad Cl^-$$

The aim of the investigation was to confirm that the compounds were salts, find out some of their physical and chemical properties, and explore the range of types of salt of the general formula $R_2M\text{-}P^+\text{-}R'R''_2 \quad X^-$ that it was possible to prepare.

SUMMARY

The compounds formed by the reaction of dialkylhalo- and diarylhalo- Group V B metals with tertiary phosphines are generally white stable crystalline salts of the type $R_2M-P^+R_3 \quad X^-$, e.g. $Me_2As-P^+Et_3 \quad I^-$. Their salt-like character has been confirmed (i) by cryoscopic measurements of their apparent molecular weight in nitrobenzene which are slightly over half the formula molecular weight; and (ii) by their conductivities in nitrobenzene.

Conductimetric titrations in nitrobenzene of arsines against phosphines have shown the range of types of compound which can be formed. Triethylphosphine readily forms salts with dimethyliodoarsine and diethyliodoarsine, however with diphenyliodoarsine the salt isolated was not very stable. The conductimetric titration results proved the 1:1 addition of arsine and phosphine and confirmed the existence of $Ph_2As-P^+Et_3 \quad I^-$. In this way it has been shown that Ph_2SbCl forms salts with PEt_3 and $PhPMe_2$ although they were not isolated. When PPh_3 was quantitatively recovered from the attempted reactions with Me_2AsCl and Me_2AsI the non-existence of the salts was subsequently confirmed by conductimetric titrations. The conductimetric titrations have shown that the donor character

of phenyldimethylphosphine towards dimethyliodoarsine is much stronger than that of pyridine, though salts were isolated in both instances.

Some salts were prepared by reacting Me_2AsI with N-methylmorpholine and 2,2'-bipyridyl; salts were also formed by reaction of trialkyltinhalides with phosphines and amines.

The salts can be handled in air for a short while; some are hygroscopic; others decompose when not kept under nitrogen. The reaction of $Me_2As\text{-}P^+PhMe_2\ I^-$ with aqueous potassium hydroxide yielded quantitatively cacodyl oxide and phenyldimethylphosphine.

The preparation and some properties are described of dimethylmethoxyarsine and dimethylphenoxyarsine which have not previously been reported.

EXPERIMENTAL

All reactions with phosphines, arsines, stibines, bismuthines, tin compounds and amines were carried out in a nitrogen atmosphere.

Phenyldimethylphosphine[1]

$$2\ MeMgI + PhPCl_2 \longrightarrow PhPMe_2$$

Methylmagnesium iodide was prepared from methyl iodide (4½ moles) in dry ether (3 l.) and excess magnesium. To the Grignard reagent at -5° was added dropwise (3 hrs.) phenyldichlorophosphine (2 moles) in ether (1 l.). After 2 hrs. the mixture was carefully hydrolysed with conc. NH_4Cl + Na_2HPO_4 solution and ether (1 l.) distillate collected. The stirrer stuck in the precipitated magnesium salts and was mechanically moved with difficulty; stirring became easier when the distilled ether was returned to the reaction mixture.

Phenyldimethylphosphine was isolated by steam distillation, dried, and redistilled. (Yield: $PhPMe_2$, 540 g., 67%, b.p. 96°/38 mm.)

Diphenylmethylphosphine

$$Ph_2PCl + Me\ MgI \longrightarrow Ph_2PMe$$

Methyl magnesium iodide (0.11 mole) was prepared in ether (70 ccs.). To the Grignard reagent surrounded by a cooling bath at -30° to -20° was added dropwise diphenylchlorophosphine (0.1 mole) in ether (50 ccs.). After water hydrolysis the slurry was filtered and the ether phase separated and dried. The Ph_2PMe solution in ether was distilled and the fraction b.p. 91°-93°/0.04 m.m. collected. (Yield: Ph_2PMe, 18 g., 90%).

Triethylphosphine[2]

$$3\ EtMgBr + PBr_3 \longrightarrow Et_3P$$

Ethyl magnesium bromide (5¼ moles) was prepared in ether (3 l.). To this was added (3 hrs.) phosphorus tribromide (1.7 moles) in ether (500 ccs.). An external cooling bath was kept throughout the PBr_3 addition at -40° to -20°. After cautious hydrolysis and steam distillation triethylphosphine was isolated. (Yield: Et_3P, 118 g., 77%, b.p. 128°).

In an earlier preparation of Et_3P the external temperature of the cooling bath used when adding PBr_3 to the Grignard reagent was at -20° to -5°. Much yellow ether insoluble material was observed and a 58% yield of Et_3P obtained. The hydrolysis must be carried out slowly with vigorous stirring and much ether present. In this way the magnesium salts precipitated will not cake so readily and less frothing will occur.

Phosphorus tribromide[3]

Bromine (9.7 moles) was run at 5 mls./min. into a boiling suspension of red phosphorus in phosphorus tribromide. (Yield: 786 g., 90%, b.p. 72°/23 mm.).

Dry red phosphorus was required for this preparation. Oven drying at 105° was inadequate but pumping at 100°/12 mm. for 2 hrs. was found satisfactory. Care must be taken not to add the bromine too quickly to combine with the red phosphorus, as excess bromine will volatilize and combine with PBr_3 to form solid PBr_5 in the reflux condenser.

Diphenylchloroarsine[4]

$$PhNHNH_2 + H_3AsO_4 \longrightarrow (Ph_2As)_2O \xrightarrow{HCl} Ph_2AsCl$$

Phenylhydrazine (1.2 moles) was run (1½ hrs.) into arsenic acid (150 ccs. tech. 75% w/w.) in water (800 ccs.) at 75° with cuprous oxide (10 g.) and copper powder (5 g.) as catalysts. The bisdiphenylarsine oxide was extracted with carbon tetrachloride (150 ccs. x 2) and then shaken (10 mins.) with conc. hydrochloric acid (100 ccs.). This solution of diphenylchloroarsine was combined with that from a similar preparation using As_2O_5 (0.94 mole) in 1 l. water with phenylhydrazine (1.5 moles). Time of addition was 4 hrs. From the CCl_4 extract was isolated by distillation,

	Ph_2AsCl	112 g.	b.p. 150°/2-3 mm. Solid at room temperature.
and	$PhAsCl_2$	80 g.	b.p. 70°-100°/2-3 mm.

<u>Diphenyliodoarsine</u>

$$Ph_2AsCl + NaI \longrightarrow Ph_2AsI$$

Diphenylchloroarsine in acetone was refluxed (3 hrs.) with an excess of sodium iodide solution in acetone. Diphenyliodoarsine was isolated as a golden crystalline sublimate. m.p. 41°.

<u>Diphenylchlorostibine</u>[5]

$$SbCl_3 \xrightarrow{PhMgBr} SbPh_3 \xrightarrow[MeOH]{HCl} Ph_2SbCl \xrightarrow{NaOH} (Ph_2Sb)O$$

$$\xrightarrow{CH_3COOH} Ph_2SbOAc \xrightarrow{HCl} Ph_2SbCl$$

To phenyl magnesium bromide (1.5 moles) in ether (750 ccs.) was added (1 hour) antimony trichloride (0.48 moles) in ether (500 ccs.). After hydrolysis, and removal of the ether by distillation, the triphenylstibine was crystallised from a mixture of ethanol (400 ccs.) and ether (100 ccs.). m.p. 49°. (Yield: Ph_3Sb, 164 g., 91%).

Triphenylstibine (164 g.) in anhydrous methanol (2 l.) was refluxed (4 hrs.) with methanol (500 ccs.) saturated with hydrogen chloride. Sodium hydroxide solution (2 N.) was added to neutralise the cooled solution at -12°. The gummy bisdiphenylstibine oxide was separated by filtration and washed with water. Then it was heated at 100° for 4 hrs. in a current of nitrogen to convert any phenylstibine oxide to bisdiphenylstibine oxide which was extracted with hot ethanol (400 ccs. x 3). The bulk of the ethanol was distilled off and acetic acid (200 ccs.) added to give a white precipitate of the acetate which was crystallised from acetic acid, m.p. 132°.

To the diphenylacetoxystibine in acetic acid (150 ccs.) was slowly added conc. hydrochloric acid (200 ccs.). A yellow oil (diphenylchlorostibine) came down and later solidified. Crystallisation from acetic acid as recommended by Blicke, Oakdale and Smith[5] was not satisfactory. Distillation gave diphenylchlorostibine 118°-122°/2 mm., bulk at 120°/2 mm. m.p. 68°. (Yield: 47 g., 32%, from $SbCl_3$).

Diphenylchlorobismuthine[6]

$$BiCl_3 \xrightarrow{PhMgBr} BiPh_3 \xrightarrow{BiCl_3} Ph_2BiCl \xrightarrow{NaI} Ph_2BiI$$

To phenyl magnesium bromide (1.07 moles) in ether (600 ccs.) was slowly added (40 mins.) bismuth trichloride (0.32 moles) in ether (500 ccs.) and benzene (200 ccs.) and then refluxed for 5½ hrs. After hydrolysis and filtration the layers were separated and the ether and benzene distilled and pumped off. The triphenylbismuthine was washed with pet. ether 40-60°. m.p. 77°. (Yield: 107 g., 76%).

Triphenylbismuthine (0.04 mole) in ether (300 ccs.) was stirred with bismuth trichloride (0.0272 mole) in ether (300 ccs.) and precipitated almost quantitatively diphenylchlorobismuthine. m.p. 185°.

Diphenylchlorobismuthine[5b] (0.058 mole) and sodium iodide (0.062 mole) in absolute ethanol (200 ccs.) were shaken for 12 hrs. and poured into boiling water (600 ccs.). Diphenyliodobismuthine was separated by filtration, washed, and dried. m.p. 134°.

Cacodyl chloride[7]

To cacodylic acid (250 g.) in conc. hydrochloric acid (447 ccs.) was added a half portion of a slurry of sodium hypophosphite (196 g.) with conc. hydrochloric acid (670 ccs.). This was stirred (1 hr.) and the temperature kept below 35°. Then the second half portion of the slurry was added and stirred for 2 hours. A pale yellow oil was separated, dried and distilled. b.p. 107°. (Yield: Me_2AsCl, 143 g., 56%).

Cacodyl bromide was prepared in a similar way to cacodyl chloride. Initially magnesium sulphate drying was unsatisfactory and the product had to be dried again after distillation.

Cacodyl iodide[8]

Sulphur dioxide was passed (12 hrs.) through a solution of cacodylic acid (500 g.), potassium iodide (1000 g.) and conc. sulphuric acid (183 ccs.) in water (4 l.) until much sulphur was deposited. The heavy yellow oil was separated, dried and distilled. b.p. 50-52°/ ~ 13 mm. (Yield: Me_2AsI, 796 g., 95%).

Phosphonium salts[9]

Dimethylarsinophenyldimethylphosphonium iodide.

$$Me_2AsI + PhPMe_2 \longrightarrow Me_2As\text{-}P^{+}PhMe_2 \quad I^{-}$$

Phenyldimethylphosphine (27.6 ccs. 0.2 mole) in ether

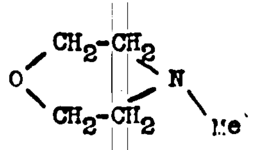
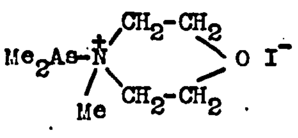
(70 ccs.) was slowly (10 mins.) run into cacodyl iodide (33.2 ccs. 0.2 mole) in ether (250 ccs.). An exothermic reaction occurred and the phosphonium salt was immediately precipitated. After stirring for 2 hours the salt was isolated and crystallised from absolute ethanol (2 l.) as white square plates. (Yield: 45.5 g., 62%, m.p. 147°.) Found: C, 32.3; H, 4.6. $C_{10}H_{17}AsIP$ requires C, 32.4; H, 4.6%.

About 30 salts were prepared in an analogous method to dimethylarsinophenyldimethylphosphonium iodide. The experimental results are summarised in the table at the back of this thesis.

The reaction of dimethylarsinophenyldimethylphosphonium iodide with aqueous potassium hydroxide

Dimethylarsinophenyldimethylphosphonium iodide (0.00902 mole) in a 50 cc. 2 neck flask was attached to a vacuum fractionating apparatus under nitrogen and the apparatus was then evacuated. Potassium hydroxide (0.027 mole) in air-free distilled water (20 ccs.) was added and as the salt dissolved an oily layer separated. Volatile material was condensed in a trap surrounded by liquid air. This was twice fractionated at -20° to remove water vapour, a gas which was liquid from -60° to -20° (high vac.) was

Organic Phosphonium salts. by J.M.F. Braddock
(M.Sc. Thesis, August 1960).

						Analyses						
						found				requires		
	PR_3	R_2MX	Salt	Solvent of crystallisation	m.p.[e]	C		H		C		H
1	PMe_3	Me_2AsI	$Me_2As\text{-}P^+Me_3\ I^-$	$EtOH/H_2O$	270-273°	20.2		5.1	$C_5H_{15}AsIP$	19.6		4.9
2	PEt_3	Me_2AsI	$Me_2As\text{-}P^+Et_3\ I^-$	EtOH	132-135	27.7		6.0	$C_8H_{21}AsIP$	27.6		6.0
3	PEt_3	Me_2AsBr	$Me_2As\text{-}P^+Et_3\ Br^-$	EtOH	142-145	31.8		7.1	$C_8H_{21}AsBrP$	31.8		7.0
4	PEt_3	Me_2AsCl	$Me_2As\text{-}P^+Et_3\ Cl^-$	$Et_2O/EtOH$	73-75	37.3		8.2	$C_8H_{21}AsClP$	37.2		8.1
5	PEt_3	$MeSbBr_2$	$Et_3P \longrightarrow SbMeBr_2$	EtOH	142-145 dec.	20.4	Br 39.1	4.2	$C_7H_{18}Br_2PSb$	20.3	Br 38.8	4.3
6	PEt_3	Ph_2AsCl	white compound	MeOH	40-41	35.9	Cl 12.9	4.0	$C_{18}H_{25}AsClP$	51.4	Br 9.3	6.5
7	PEt_3	Ph_2AsI	$Ph_2As\text{-}\overset{+}{P}Et_3\ I^-$	EtOH	85-87	45.4		5.6	$C_{18}H_{25}AsIP$	45.4		5.3
8	PEt_3	Ph_2SbI,Cl	Not isolated									
9	PEt_3	Ph_2BiI,Cl	Not isolated									
10	PEt_3	Me_3SnBr	white compound	washed hexane	53-55	23.5		5.9	$C_9H_{24}BrPSn$	29.9		6.6
11	PEt_3	Et_3SnI,Cl	no reaction									
12	PPr_3^n	Me_2AsI	$Me_2As\text{-}P^+Pr_3^n\ I^-$	Pr^nOH	100	33.2		6.9	$C_{11}H_{27}AsIP$	33.7		6.9
13	$PPhMe_2$	Me_2AsI	$Me_2As\text{-}P^+PPhMe_2\ I$	EtOH	147	32.3		4.6	$C_{10}H_{17}AsIP$	32.4		4.6
14	$PPhMe_2$	Me_2AsBr	$Me_2As\text{-}P^+PhMe_2\ Br^-$	EtOH	178	38.3		5.6	$C_{10}H_{17}AsBrP$	37.3		5.3
15	$PPhMe_2$	Me_2AsCl	$Me_2As\text{-}P^+PhMe_2\ Cl^-$	Me_2CO	115-116	43.6		6.2	$C_{10}H_{17}AsClP$	43.3		6.1
16	$PPhMe_2$	Et_2AsI	$Et_2As\text{-}P^+PhMe_2\ I^-$	EtOH	112-118	36.4		5.5	$C_{12}H_{21}AsIP$	36.3		5.3
17	$PPhMe_2$	$MeSbBr_2$	$PhMe_2P \longrightarrow SbBr_2Me$	EtOH	175-176 dec.	24.9		3.1	$C_9H_{14}Br_2PSb$	24.9		3.2
18	$PPhMe_2$	Ph_2AsCl	white compound	Me_2CO	126	56.6	Cl 14.1	8.0	$C_{20}H_{21}AsClP$	59.8	Cl 8.8	5.2
19	$PPhMe_2$	Ph_2AsI	$Ph_2As\text{-}\overset{+}{P}PhMe_2\ I^-$	EtOH	107-108							
20	$PPhMe_2$	Ph_2SbI,Cl	Not isolated[9]									
21	$PPhMe_2$	Ph_2BiI,Cl	Bi and $BiPh_3$ isolated									
23	$PPhMe_2$	Et_3SnI,Cl	No reaction									
24	$PPhEt_2$	Me_2AsBr	$Me_2As\text{-}P^+PhEt_2\ Br^-$	Pr^nOH	142-148	41.3		6.3	$C_{12}H_{21}AsBrP$	41.1		6.0
25	PPh_2Me	Me_2AsI	$Me_2As\text{-}P^+Ph_2Me\ I^-$	EtOH	115-117	42.1		4.5	$C_{15}H_{19}AsIP$	41.7		4.4
26	PPh_3	Me_2AsI	PPh_3 recovered 95%									
27	PPh_3	Me_2AsCl	PPh_3 recovered 91%									
28	C_5H_5N	Me_2AsI	$Me_2As\text{-}N^+C_5H_5\ I^-$	EtOH	194 dec.	28.6	I 39.0	3.3	$C_7H_{11}AsIN$	27.1	I 40.9	3.5
29	C_5H_5N	Me_3SnBr	$Me_3Sn\text{-}N^+C_5H_5\ Br^-$	washed hexane	64	29.8		4.8	$C_8H_{14}BrNSn$	28.9		4.2
30	$(C_5H_4N)_2$	Me_2AsI	white compound	would not crystallise		no analysis						
31	$(C_5H_4N)_2$	Me_3SnBr	not isolated									
32		Me_2AsI		EtOH	113	25.3		5.1	$C_7H_{17}AsINO$	26.2		5.8

a. The conductimetric titration results were worked out graphically, curved graphs were obtained at the end point. See graphs III, IV and V.

b. The considerable curve at the end point also indicated that a 1 C_5H_5N:2 Me_2AsI compound could exist. See graph V.

c. The conductimetric titration results showed an increase in conductivity indicating salt formation. The graphs were very curved and no equivalent ratios could be obtained from them.

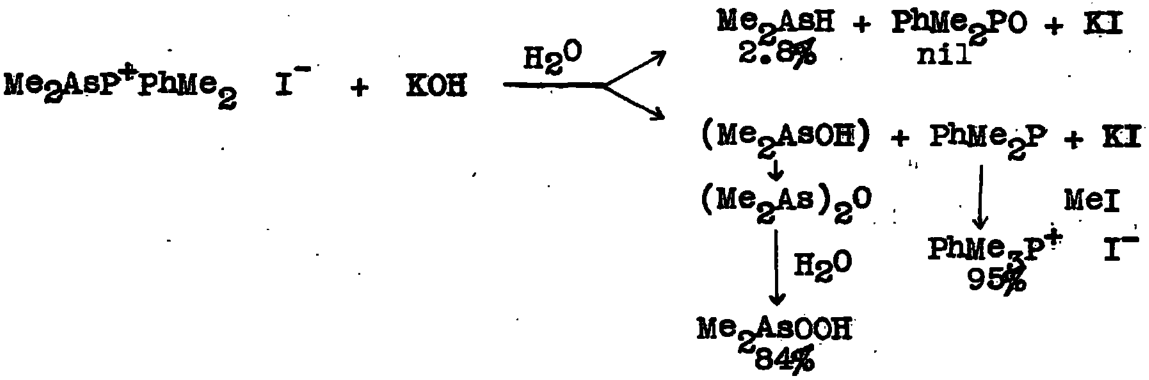
d. A solution of $Et_3P \longrightarrow SbMeBr_2$ in nitrobenzene had a low conductance. The bromine present was not ionic as silver bromide was slowly precipitated from an aqueous acetone solution of the compound by silver nitrate.

e. The melting points obtained were the results of using a stem corrected thermometer. The salt crystals softened at the lower quoted temperature range and then melted. The melt usually slowly decomposed and distilled off.

isolated. The infra-red spectrum indicated aliphatic C-H present, there was a strong smell of arsine, and a white residue was left on aerial oxidation. 5.6 N-c.c. of gas were collected which would correspond to Me_2AsH 0.00025 mole, yield 2.77%.

Water vapour was condensed back into the original flask which was taken off the system and an ether extraction (50 ccs. x 2) carried out. No $PhMe_2PO$ was detected in the aqueous phase. To the ether phase was added methyl iodide and phenyltrimethylphosphonium iodide (0.0086 mole) was precipitated immediately. Hydrogen peroxide (50 vols.) was added to the ether filtrate and cacodylic acid (0.008 mole) was isolated.

reaction:-



Dimethylmethoxyarsine

$$Me_2AsI + NaOMe \longrightarrow Me_2AsOMe$$

Solid sodium methoxide (0.176 mole) and cacodyl iodide (0.08 mole) in xylene (120 ccs.) was refluxed (4 hrs.) until the colour of the Me_2AsI had disappeared. From the third fractional distillation, using an 8" lagged column packed with glass helices, was collected a clear oil b.p. 79°. Me_2AsOMe (.0938 mole) gave after vigorous hydrolysis and oxidation with H_2O_2 ~~AsOOH~~, Me_2AsO_2H (0.0936 mole).

White trimethylmethoxyarsonium iodide was formed by the addition of methyl iodide to an ethereal solution of dimethylmethoxyarsine. The salt immediately (1 min.) turned yellow in air. m.p. 85°. (yellow from 60°) Found: C, 17.3; H, 4.6; I, 45.0. $C_4H_{12}AsIO$ requires C, 17.3; H, 4.3; I, 45.7%.

Dimethylphenoxyarsine.

$$PhOH + Na \longrightarrow PhONa \xrightarrow{Me_2AsI} PhOAsMe_2$$

To sodium phenoxide (0.1 mole) (excess PhOH sublimed out) in tetrahydrofuran (65 ccs.) was added cacodyl iodide (0.08 mole). A white precipitate formed and the colour of the cacodyl iodide almost disappeared. Dimethylphenoxyarsine distilled with some decomposition at 204°. This was redistilled 101°/ ~ 12 mm. (water pump). Found: C, 49.5; H, 5.6. $C_8H_{11}AsO$ requires C, 48.5; H, 5.8%.

$PhOAsMe_2$ (0.0662 mole) on hydrolysis and bromination gave tribromophenol (0.0662 mole).

From attempts to form trimethylphenoxyarsonium iodide by the addition of methyl iodide to dimethylphenoxyarsine was isolated tetramethylarsonium iodide m.p. 349°.

Cryoscopic determinations of apparent molecular weight

The freezing point determinations were carried out in a lagged apparatus designed to give reproducible cooling conditions. Nitrobenzene* was a suitable ionising solvent for the apparent molecular weight measurements of the phosphonium salts. The freezing point constant K for the nitrobenzene was found using p-nitrotoluene at 5 concentrations. K = 70.9. Weighed quantities of the compound were added to a weighed sample of nitrobenzene and the mean of three readings of the freezing point of the solution taken. Concentrations were varied to give values for freezing point depressions up to 0.5° on the Beckmann thermometer. A slow stream of nitrogen was passed to prevent aerial oxidation or hydrolysis of the phosphonium salt and the absorption of atmospheric water vapour into the very hygroscopic nitrobenzene. A few pellets of "Linde"

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* Nitrobenzene was purified by P_2O_5 drying, two distillations under reduced pressure, and two fractional crystallisations.

molecular seive type 5A $\frac{1}{8}$" were added to absorb any water which did go into the nitrobenzene. The nitrogen flow must not be too fast as nitrobenzene vapour is blown off and the temperature equilibrium conditions upset.

Dimethylarsinotriethylphosphonium iodide (I)

Molecular weight 350. K = 70.9 for nitrobenzene.

g.(I)	g. $PhNO_2$	Δt^o	Molality	Apparent M.
.0814	37.06	.085	.0063	183
.2828	37.06	.266	.0222	203
.4510	37.06	crystallisation of (I) before freezing point.		

Dimethylarsinophenyldimethylphosphonium iodide (II)

Molecular weight 370.

g.(II)	g. $PhNO_2$	Δt^o	Molality	Apparent M.
.1879	32.49	0.156	0.0156	262
.5578	32.49	crystallisation of (II) before freezing point.		

Dimethylarsinotri-n-propylphosphonium iodide (III)

Molecular weight 392.

g.(III)	g. $PhNO_2$	Δt^o	Molality	Apparent M.
.1456	26.49	.150	.0143	260
.539	31.54	.425	.0437	285
.888	35.99	.588	.0623	297

Conductivity of phosphonium salts

The cell constant of the conductivity measuring cell was found by measuring the resistance of a 0.01 N potassium chloride solution in conductivity water at 25°. Cell constant = 0.1690.

The phosphonium salt was twice recrystallised and a known quantity dissolved in a known weight of pure nitrobenzene in a weight pipette under nitrogen, and placed in a thermostat at 25°. A known weight of nitrobenzene was put in the conductivity cell which was in the thermostat. From the weight pipette known quantities of the phosphonium salt solution were added to give solutions in the concentration range 0.5 to 6 x 10^{-3} molal. The mean of four resistance readings at 5 minute intervals was taken to calculate conductivity values which were graphically plotted against the square root of the molality.

At concentration 1 x 10^{-3} molal the molal conductivity of $Me_2As-P^+Et_3\ \ I^-$ = 36.93 mhos. and of $Me_2As-P^+PhMe_2\ \ I^-$ = 32.47 mhos.

See graph I.

Conductimetric titrations

The method is illustrated by the description of an experiment where cacodyl iodide was titrated against phenyldimethylphosphine. For apparatus see diagram I. A solution of the arsine (of known molality) was prepared in nitrobenzene, and after its density had been measured the solution was placed in a burette. Phosphine solution of known molality was weighed from a weight pipette into a known weight of nitrobenzene in the conductivity cell in a thermostat at 25°. The arsine was then added 1 c.c. at a time and the resistance of the solution measured. Some titrations were carried out at room temperature and a magnetic stirrer was used; the quantity of nitrobenzene in the cell was not accurately known in some of the earlier experiments. Results for the conductimetric titration of cacodyl iodide against phenyldimethylphosphine at 25° in a known weight of nitrobenzene:

0.7045 g. Me_2AsI in 34.3804 g. $PhNO_2$. $D^{25} = 1.22$.

16.981 g. $PhNO_2$ in cell to which was added 5.7928 g. of solution of .0938 g. $PhPMe_2$ in 6.1181 g. $PhNO_2$ i.e. 0.0006339 mole of phosphine.

ccs. Me_2AsI	moles Me_2AsI	R x 10^3 ohms	$K = \frac{.169 \times 1000}{R}$ mhos.
1	.0001056	.917	.1843
2	.0002112	.592	.2855
3	.0003168	.481	.3514
4	.0004224	.432	.3912
5	.0005280	.402	.4204
6	.0006336	.398	.4246
7	.0007392	.402	.4204
8	.0008448	.410	.4122
9	.0009504	.420	.4024
10	.0010560	.432	.3912

The specific conductance K was plotted against the number of moles of arsine. See graph III.

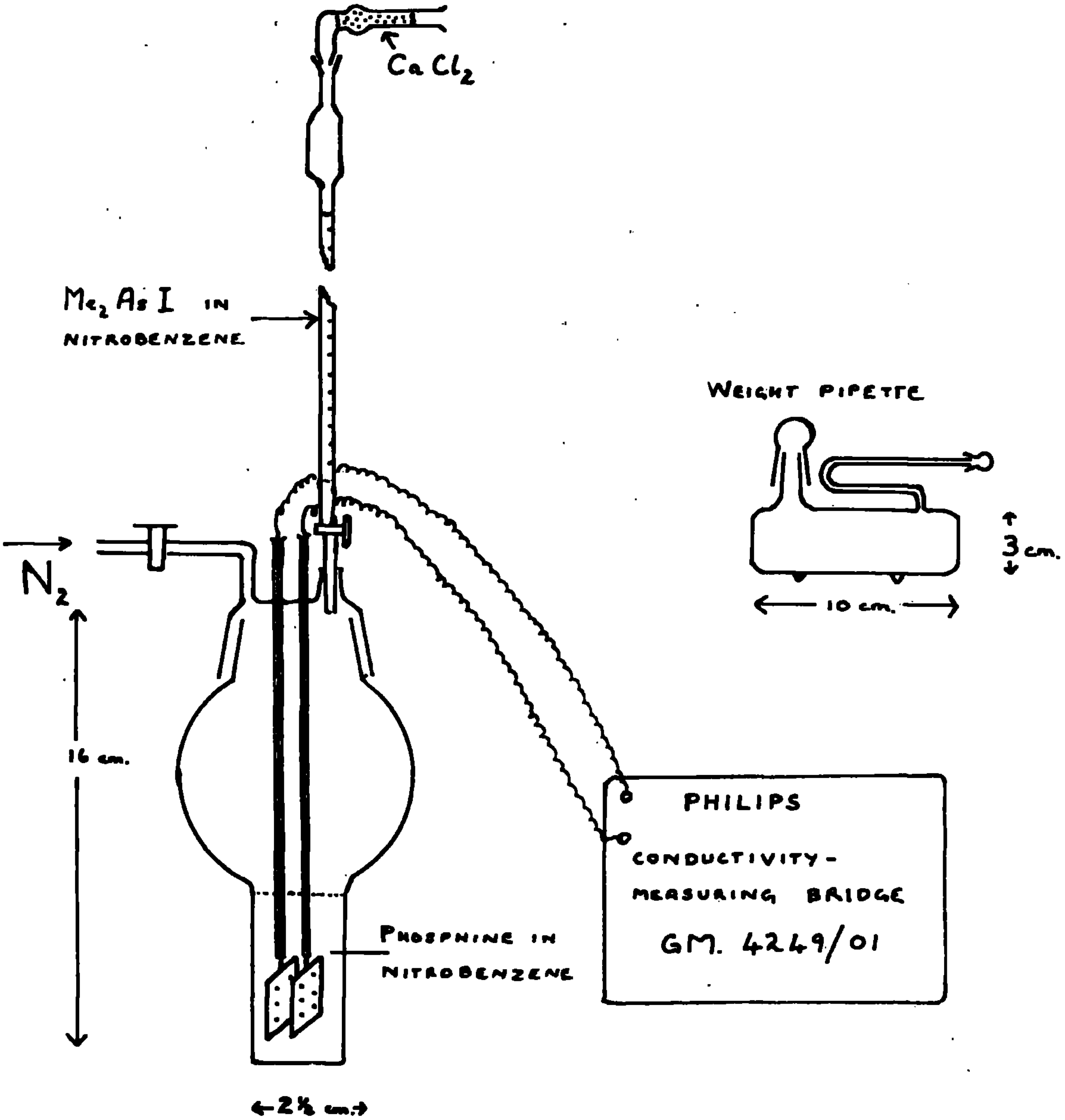
0.0006339 moles $PhPMe_2$ ≡ 0.00066 moles Me_2AsI

1 mole of phosphine ≡ 1.03 mole of arsine.

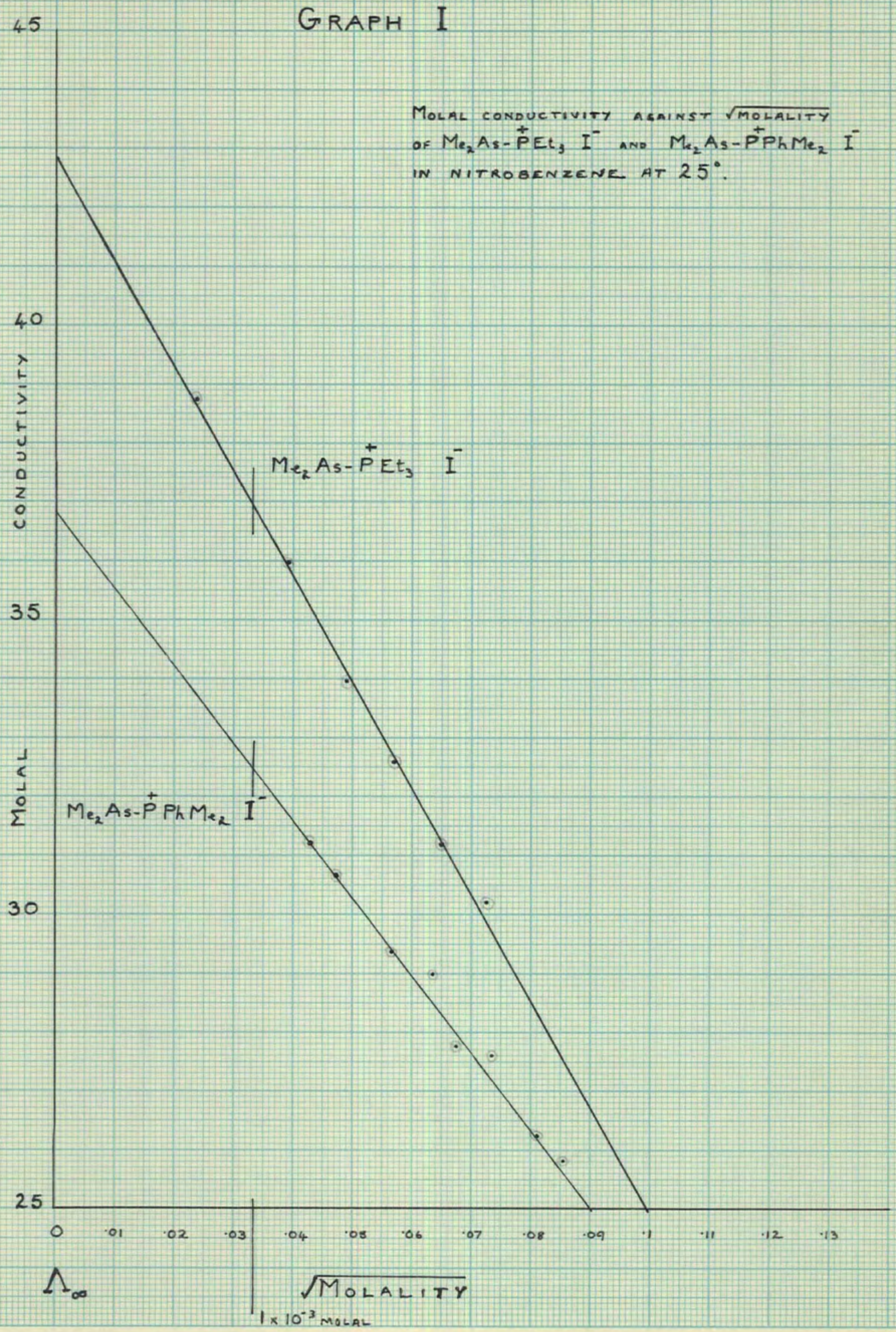
The results of the conductimetric titrations of Me_2AsI with PEt_3, Ph_2PMe and C_5H_5N are shown on graphs II, IV and V. Other conductimetric titration results are summarised in table I.

FIGURE I

Conductimetric titration apparatus.



The conductivity cell was placed in a thermostat at 25°.

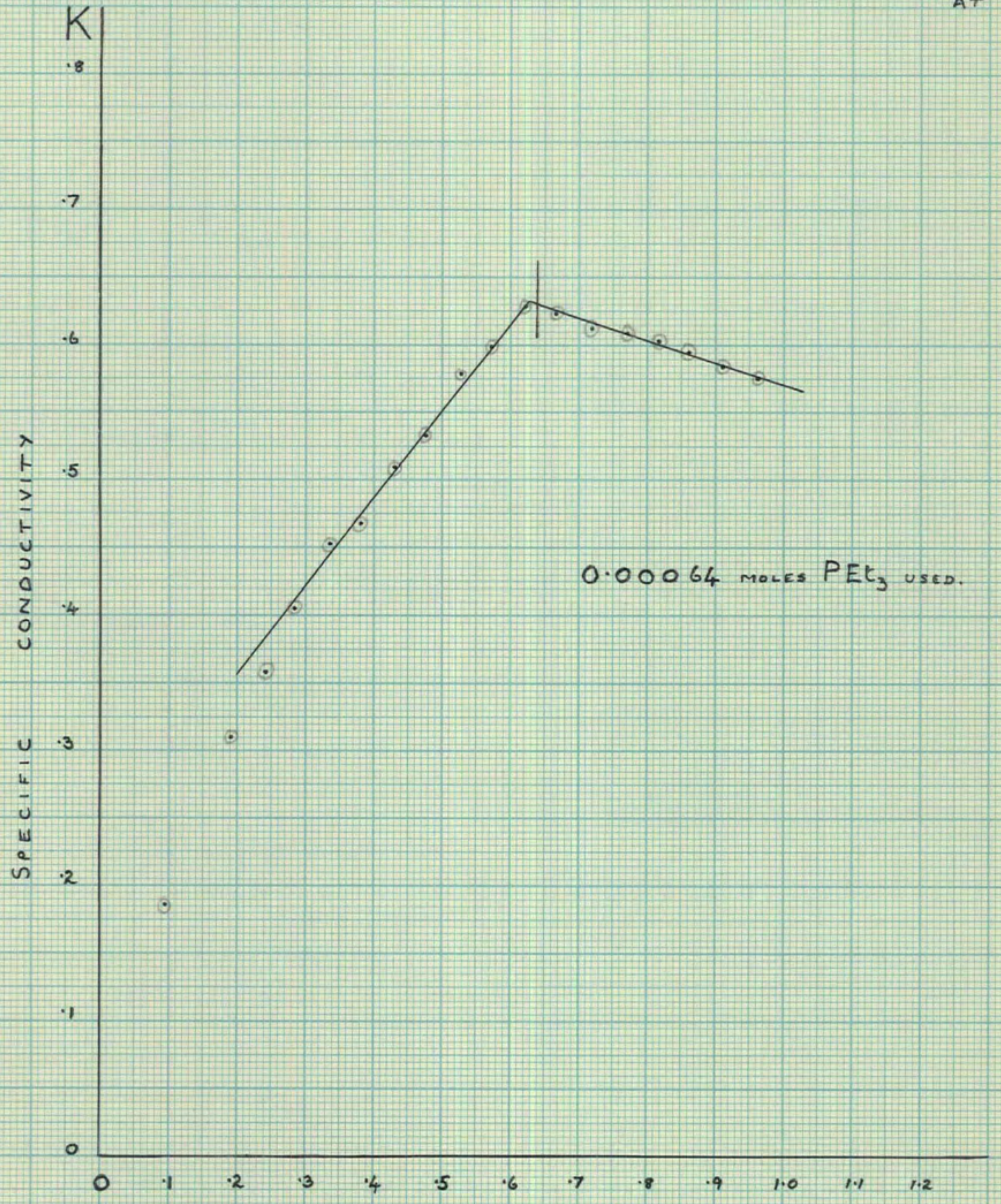


GRAPH I

MOLAL CONDUCTIVITY AGAINST $\sqrt{\text{MOLALITY}}$ OF $Me_2As\text{-}\overset{+}{P}Et_3\ \overset{-}{I}$ AND $Me_2As\text{-}\overset{+}{P}PhMe_2\ \overset{-}{I}$ IN NITROBENZENE AT 25°.

GRAPH II

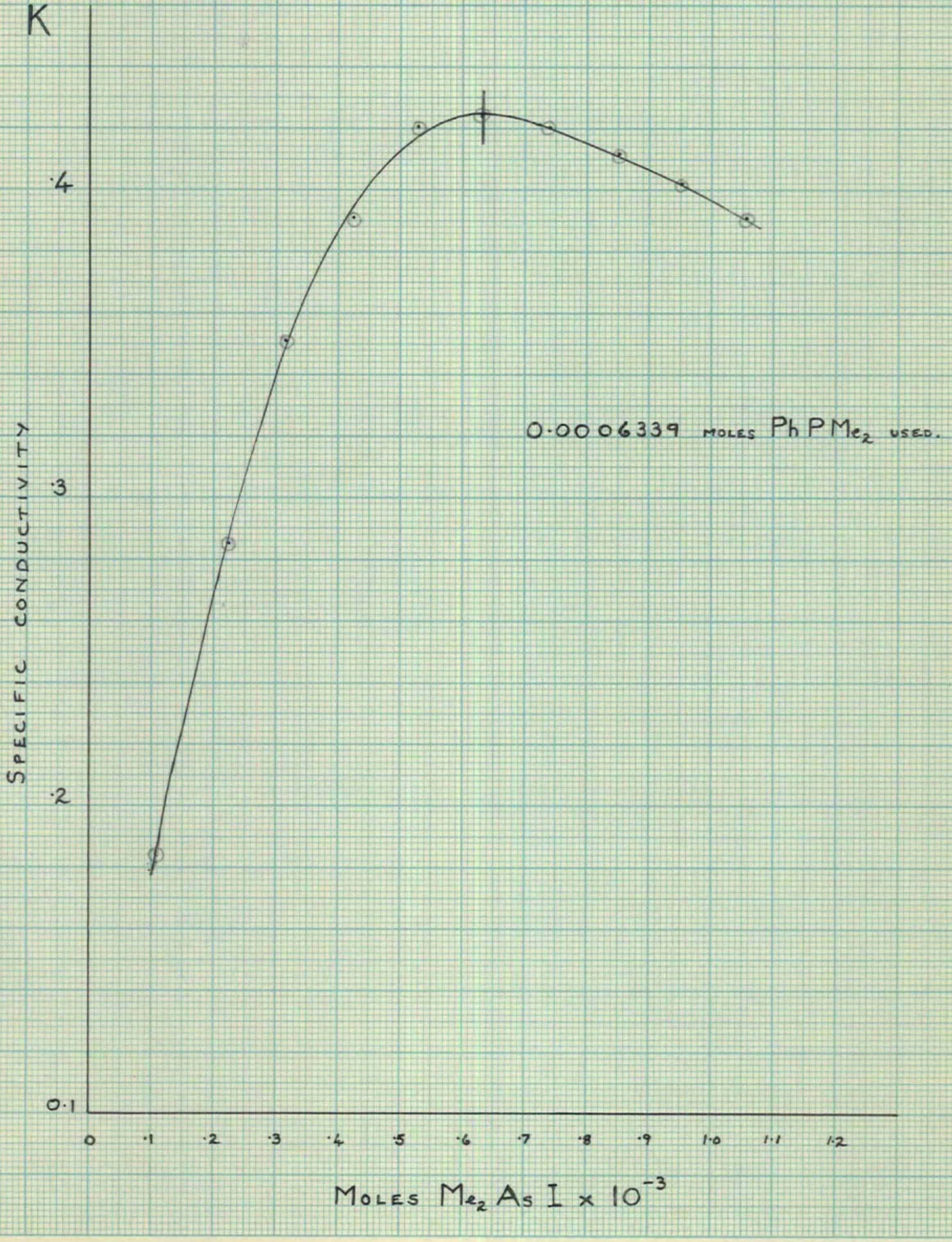
CONDUCTIMETRIC TITRATION Me_2AsI AGAINST PEt_3 IN $PhNO_2$ AT 25°.



MOLES $Me_2AsI \times 10^{-3}$.

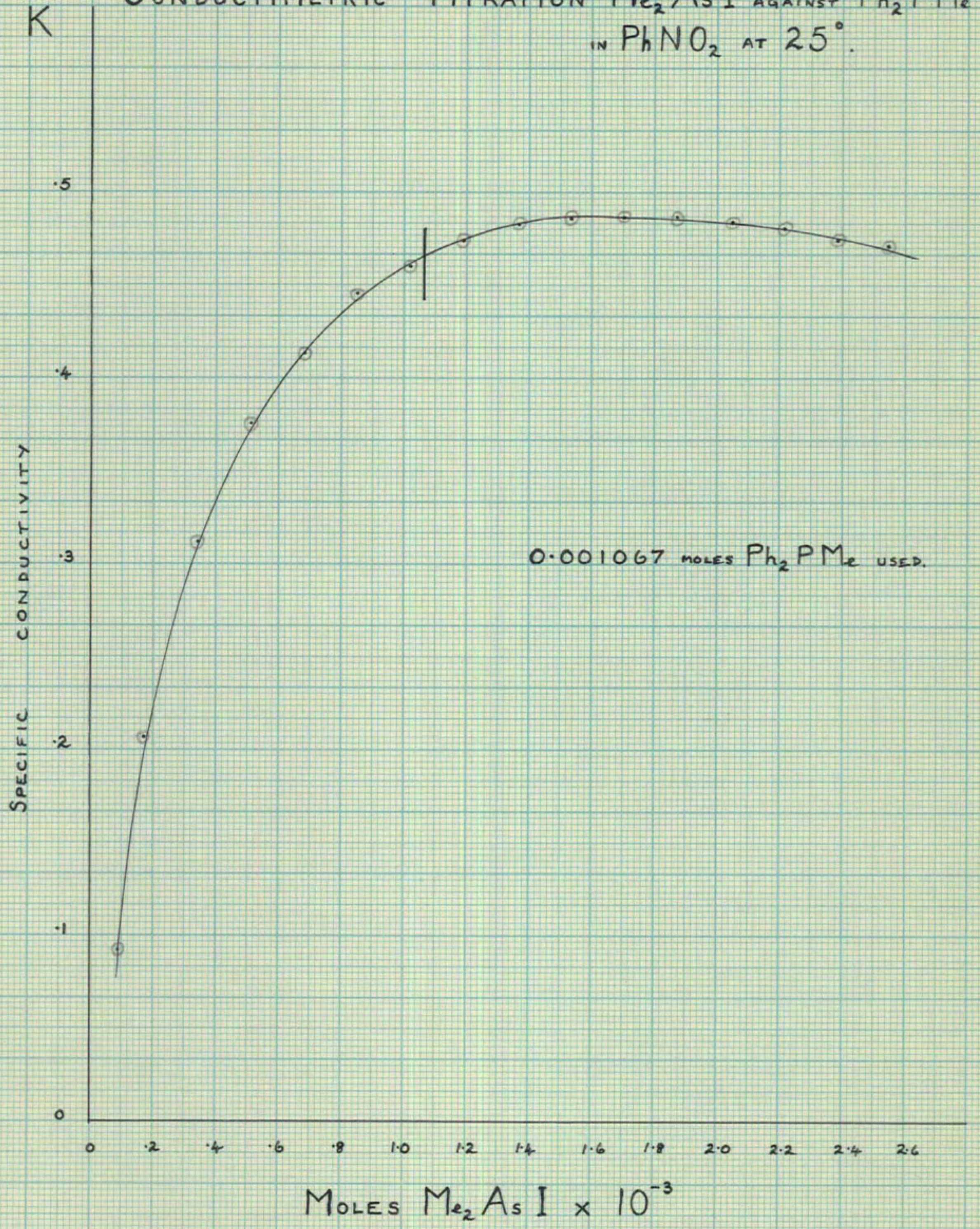
GRAPH III

CONDUCTIMETRIC TITRATION Me_2AsI AGAINST $PhPMe_2$ IN $PhNO_2$ AT 25°.



GRAPH IV

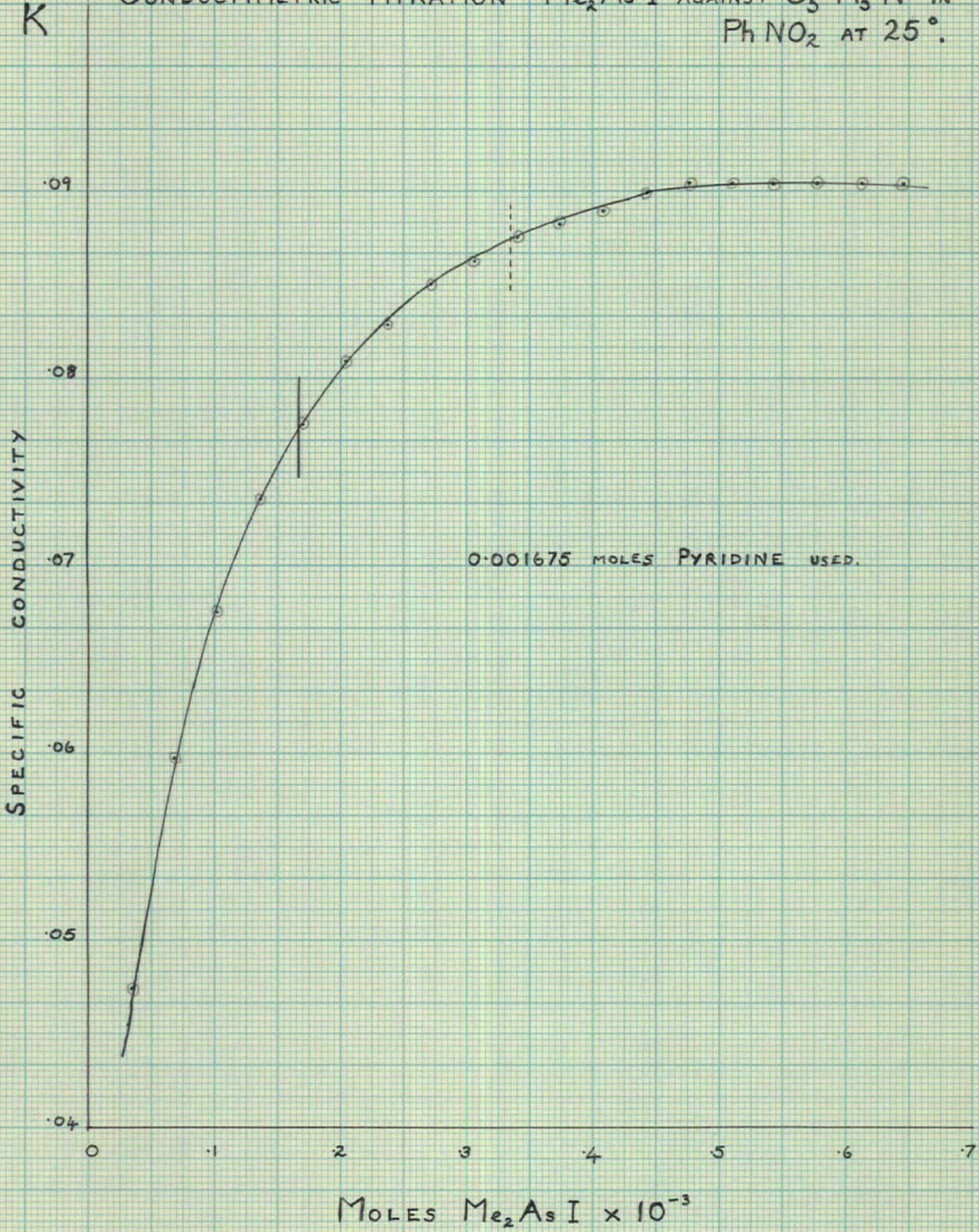
CONDUCTIMETRIC TITRATION Me_2AsI AGAINST Ph_2PMe IN $PhNO_2$ AT 25°.



0·001067 MOLES Ph_2PMe USED.

GRAPH V

CONDUCTIMETRIC TITRATION Me_2AsI AGAINST C_5H_5N IN $PhNO_2$ AT 25°.



DISCUSSION

Preparative aspects

The compounds formed by the general reaction $R_2MX + PR_3 \longrightarrow R_2M\text{-}P^+R_3 \quad X^-$ are white crystalline salts. They are insoluble in non-polar solvents such as benzene and hexane, often slightly soluble in weakly polar solvents such as ether and tetrahydrofuran, and soluble in strongly polar solvents such as ethanol, acetone and water. They are usually best crystallised from ethanol. While some compounds, e.g. $Me_2As\text{-}P^+Me_3 \quad I^-$ m.p. 270-273°, are stable to air and water, other salts, e.g. $Ph_2As\text{-}P^+Et_3 \quad I^-$ m.p. 85-87°, decompose slowly in air by hydrolysis and oxidation. Some chlorides e.g. $Me_2As\text{-}P^+Et_3 \quad Cl^-$, are deliquescent and are not so stable as the iodides. Some iodides can be sublimed in vacuo presumably by reversible dissociation like the phosphonium and ammonium halides. All the salts described are stable when kept under nitrogen.

The dimethylarsinophosphonium salts react with bases e.g. sodium methoxide, to give the tertiary phosphine and the ester of dimethylarsinous acid. Reaction with alkoxide ion could possibly take either of the two courses:-

$$\text{(I)} \quad Me_2As\text{-}P^+R_3 \quad X^- + NaOR' \longrightarrow Me_2As\text{-}P^+R_3 \quad \overline{O}R' \longrightarrow$$

$$Me_2AsR' + R_3PO$$

(II) $Me_2As{-}P^+R_3 \quad X^- \rightleftharpoons PR_3 + Me_2AsX \xrightarrow{NaOR'} Me_2AsOR'$

Hey and Ingold[10] in their study of the thermal decomposition of tetralkylphosphonium alkoxides reported reactions of the type:-

$$Me_4P^+ \quad OEt^- \longrightarrow Me_3PO \; + \; C_3H_8$$

A possible mechanism likely for the decomposition involved a quinquevalent phosphorus complex,

$$R_4P^+ \quad OR^- \longrightarrow R_4P{\cdot}OR' \longrightarrow R_3PO \; + \; RR'$$

Information on the decomposition of quaternary phosphonium salts in basic solutions to give tertiary phosphine oxides has been included in a revue by Berlin and Butler.[17] They summarise numerous publications on the subject of this reaction (I), which, they conclude, is a good method for preparing tertiary phosphine oxides. Likewise the action of potassium hydroxide on phosphonium salts of the type $R_3P^+{-}NH_2 \quad Cl^-$ easily gave tertiary phosphine oxides.[18] The strong affinity of alkylphosphines for oxygen is well known. Thus there was some reason to expect that the reaction between bases and dimethylarsinophosphonium salts would proceed in a similar way, with the formation of a tertiary phosphine oxide and a secondary or tertiary arsine (reaction I above).

Preliminary investigations on the hydrolysis (by water or OH^- ion) of these salts were aimed at identifying dimethylarsine as dimethylarsinic acid (by oxidation).

Experiments in which dimethylarsinophosphonium salts were allowed to react with alkoxide (or aryloxide) ions were expected to result in the formation of tertiary arsine. Attempts were made to isolate such products as quaternary arsonium salts, by treatment of the reaction product with methyl iodide. These experiments gave confusing and unsatisfactory results because, as was later discovered, reaction in fact proceded mainly by formation of tertiary phosphines and of dimethylarsinous esters. Treatment of these with methyl iodide yielded mixtures of products which were difficult to separate[11]. In later experiments with hydrolysis of $Me_2As\text{-}P^+PhMe_2 \quad I^-$ with aqueous potassium hydroxide gave phenyldimethylphosphine and bis-dimethylarsineoxide practically quantitatively as $PhMe_3P^+ \quad I^-$ and Me_2AsO_2H. Thus reaction II was confirmed.

Since the hydrolysis of a halodimethylarsine (Me_2AsX) is, beyond reasonable doubt, sure to be a much faster reaction than the attack of OH^- or OR^- on a phosphonium cation, the most likely reason for the formation of phosphines (rather than phosphine oxides) in the hydrolysis of dimethylarsinophosphonium salts is the reversible dissociation of the latter.

$$Me_2As\text{-}\overset{+}{P}R_3 \quad X^- \rightleftharpoons Me_2AsX + PR_3$$

$$Me_2AsX + OH^- \rightleftharpoons (Me_2As)_2O + X^- + H_2O.$$

Only a small degree of dissociation is necessary to account for the hydrolysis following this path. In those instances, normally tetra-alkylphosphonium salts, in which hydrolysis yields the tertiary phosphine oxide, dissociation

$$Alkyl_4\overset{+}{P} \quad \overset{-}{X} \rightleftharpoons Alkyl_3P + Alkyl\ X$$

can safely be regarded as quite negligible.

That dissociation of dimethylarsinophosphonium salts is quite appreciable in several instances is clearly shown by the conductimetric experiments described later.

The base-promoted elimination reaction used by Grayson, Keough and Johnson[12] for the preparation of some phosphines could proceed by a similar mechanism:-

$$(NC\cdot CH_2\cdot CH_2)_3MeP^+ \quad I^- \xrightarrow{NaOEt} (NC\cdot CH_2\cdot CH_2)_2PMe + EtOCH_2CH_2CN$$

Some reactions of sodium methoxide and phenoxide on dimethylarsinophosphonium salts were carried out. From these reactions tertiary phosphines and dimethylmethoxyarsine and dimethylphenoxyarsine were isolated. To confirm that dimethylarsinous esters were reaction products, as they had not previously been described, specimens of them were prepared by the reaction:-

$$Me_2AsI \ + \ NaOR' \longrightarrow Me_2AsOR' \ + \ NaX$$

Both Me_2AsOMe and Me_2AsOPh are rapidly hydrolysed and oxidised as is the methiodide $Me_3(MeO)As^+ \quad I^-$. Tetramethylarsonium iodide was isolated from the reaction of MeI with Me_2AsOPh.

Evidence for the salt-like character of the compounds was provided by the cryoscopic measurements of their apparent molecular weights in nitrobenzene. For total ionisation the observed apparent molecular weight should be, neglecting ionic interaction, half the formula weight. The formula weight of $Me_2As{-}P^+Et_3 \quad I^-$ is 350, its apparent molecular weight is 183 at molality 0.0063, and 203 at molality 0.0222. Unfortunately stronger solutions of the salt crystallised out of nitrobenzene before the freezing point, and this happened still more readily in the case of $Me_2As\text{-}P^+PhMe_2 \quad I^-$. A series of results was obtained for the more soluble $Me_2As\text{-}P^+Pr_3^n \quad I^-$ whose formula weight is 392. Its apparent molecular weight is 260 at molality 0.0143, 285 at 0.0437, and 297 at molality 0.0623.

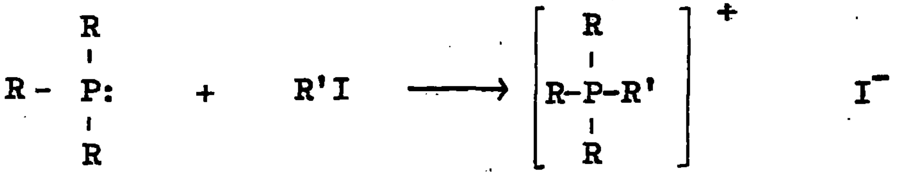
Electrical conductivities of solutions of two salts in nitrobenzene at 25° were measured. At 1×10^{-3} molal concentration the molal conductivity of:-

$$Me_2As\text{-}P^+Et_3 \quad I^- = 36.9 \text{ mhos.}$$

and $$Me_2As\text{-}P^+PhMe_2 \quad I^- = 32.5 \text{ mhos.}$$

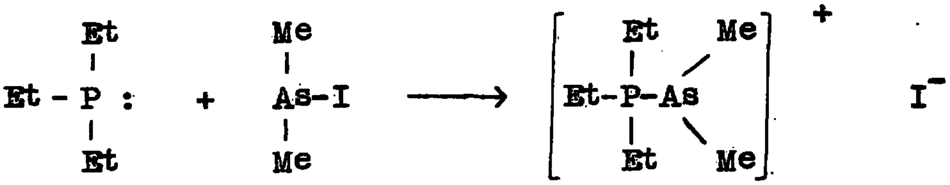
Kabesh and Nyholm[13] record that for a number of uni-univalent electrolytes in nitrobenzene at 1×10^{-3} molal concentration at 20° the molal conductivity values were in the order of 20 to 30 mhos. Although the values obtained are somewhat high they are evidence that the salts are dissociated into two ions in nitrobenzene solution. Kabesh and Nyholm's salts were all 1:1 electrolytes with relatively large ions likely to have lower mobilities than the iodide ion.

The bimolecular nucleophilic substitution type of reactions used to prepare these salts have been extensively studied.



$$R_3P: + R'I \longrightarrow \left[R_3PR'\right]^+ \quad I^-$$

By analogy the phosphonium salts described in this thesis can be expected to be formed in the same way.



$$Et_3P: + Me_2AsI \longrightarrow \left[Et_3P\text{-}AsMe_2\right]^+ \quad I^-$$

Experimental results have shown that the tendency to form salts with Me_2AsI decreases in the series $Me_3P > Et_3P > PhPMe_2 > Ph_2PMe > Ph_3P$. Likewise phosphines decrease in basicity in this series[16] and the failure of triphenylphosphine to react can reasonably be attributed to its low basicity, which is a measure of its ability to donate electrons.

It was found that the tendency to form salts with phosphines decreases in the series $Me_2AsI > Et_2AsI > Ph_2AsI$. This can be explained if an intermediate compound of the type $R_3P \longrightarrow AsR'_2X$ is formed and this is followed by ionisation:

$$R_3P \longrightarrow AsR'_2X = R_3P^+AsR'_2 \quad X^-$$

For example in Ph_2AsI the phenyl group is polarisable as well as bulky and thus it can be expected to be a weaker acceptor than Me_2AsI. The size of the steric and polar effects is theoretically difficult to predict.

The apparent greater reactivity to water and air of the chlorides than the iodides is probably because the chlorides are soluble in water to the extent of being hygroscopic.

Some supposed Me_2SbBr (left by D. Blake, formerly of this department) was redistilled, b.p. 60-80°/1-1.5 m.m.; it slowly solidified at room temperature. Samples of the solid were allowed to react with PEt_3 and $PhPMe_2$. From the reactions were isolated addition compounds, the analyses agreeing with $MeBr_2SbPEt_3$ and $MeBr_2SbPPhMe_2$. It was most likely that the stibine was in fact $MeSbBr_2$ (m.p. 42°; no information available on its boiling point) rather than Me_2SbBr m.p. 89°; b.p. 175-180°/750 m.m.). For $MeBr_2SbPEt_3$ in nitrobenzene at 25° the molal conductance values were 3.75 to 2.5 mhos at concentrations 0.000225 to 0.00326 molal. Silver bromide was only slowly precipitated on adding silver nitrate to an acetone solution of the compound. Thus the compound was not a salt, but was evidently a co-ordination complex $Et_3P \longrightarrow SbMeBr_2$.

Compounds such as $Me_3Sn{-}N^+C_5H_5 \quad Cl^-$ [14] are well known. Some analogous salts, such as $Me_3Sn{-}N^+C_5H_5 \quad Br^-$ and $Me_2As{-}N^+C_5H_5 \quad I^-$, have been prepared in the course of the present work.

Conductimetric titrations

The electrical conductivity titrations in nitrobenzene have served to show the formation of salts which were either not experimentally isolated or could not be purified. e.g. $Ph_2As{-}P^+Et_3 \quad Cl^-$, $Ph_2Sb{-}P^+Et_3 \quad Cl^-$.

An impure compound which easily decomposed was isolated from the reaction of PEt_3 with Me_3SnBr. The conductimetric titration and its properties in organic solvents suggest that a salt was formed, but analysis did not confirm the existence of $Me_3Sn{-}P^+Et_3 \quad Br^-$. Conductimetric titrations of Et_3SnCl (I) with tertiary phosphines in nitrobenzene show an increase in conductivity and the possible existence of such salts.

The conductivity titrations have shown that the donor character of $PhPMe_2$ towards Me_2AsI is much greater than that of pyridine. This is in agreement with the work of Davies and Lewis[15] insofar as they found that rates of quaternisation of tertiary phosphines with alkyl halides was greater than those of corresponding tertiary amines.

In the titration graphs (nos. II to V) of Me_2AsI forming salts with II, Et_3P; III, $PhPMe_2$; IV, Ph_2PMe; and V, C_5H_5N there is a tendency for the graph in the region of the end point to be more curved in the series II < III < IV < V.

The titration graph II of moles of Me_2AsI against the specific conductivity of the reaction mixture with Et_3P is a straight line graph showing a good end point. This is characteristic of salt formation. i.e. $Me_2AsI + PEt_3 \longrightarrow Me_2As\text{-}P^+Et_3 \quad I^-$.

However the curved titration graphs of Me_2AsI reacting with III, $PhPMe_2$; IV, Ph_2PMe; and V, C_5H_5N suggest that not all the reaction products were ionised or that reaction was incomplete. Thus the possibility that the ions were in equilibrium, either (a) with undissociated salt, or (b) with some of the original reactants, was considered.

For example in the reaction of Me_2AsI with $PhPMe_2$:-

(a) $Me_2AsI + PhPMe_2 \longrightarrow Me_2PhP^+\text{-}\overset{-}{A}sMe_2I \underset{Ka}{\rightleftharpoons} Me_2As\text{-}\overset{+}{P}PHMe_2 + I^-$

and (b) $Me_2AsI + PhPMe_2 \underset{Kb}{\rightleftharpoons} Me_2As\text{-}P^+PhMe_2 + I^-$

For equilibrium (a):-

$$K_a = \frac{[Me_2As\text{-}PPh\overset{+}{M}e_2]\ [I^-]}{[Me_2IAsPPhMe_2]}$$

and for equilibrium (b):-

$$K_b = \frac{[Me_2As\text{-}PPh\overset{+}{M}e_2]\ [I^-]}{[Me_2AsI]\ [PhPMe_2]}$$

Calculations were carried out on the results of the conductimetric titrations of Me_2AsI with $PhPMe_2$, Ph_2PMe and C_5H_5N to find out whether the equilibrium was of the type (a) or (b).

(a) The titration of Me_2AsI with $PhPMe_2$ was considered.

$$K_a = \frac{[Me_2As\text{-}PPh\overset{+}{M}e_2]\ [I^-]}{[Me_2IAsPPhMe_2]}$$

To test the existence of this equilibrium possible values were arbitrarily selected for the equilibrium constant e.g. $K_a = 0.1, 0.01$; and for each specific conductivity value the number of moles of dissociated salt were worked out and graphically plotted. For none of the arbitrary values of K_a did the calculated concentrations of dissociated salt form a straight line graph when plotted against the observed specific conductivities. Thus equilibrium between the ions and undissociated addition compound was assumed not to be significant. A similar result was obtained for the titration of Me_2AsI against Ph_2PMe. The assumption was made that the reaction between the arsine and phosphine went to completion.

(b) Once again the titration

$$Me_2AsI + PhPMe_2 \rightleftharpoons Me_2As\text{-}P^+PhMe_2 \quad I^-$$

was considered and calculations were made on the basis of the second equilibrium (K_b):

$$K_b = \frac{[Me_2As\text{-}PPhMe_2^+]\ [I^-]}{[Me_2AsI]\ [PhPMe_2]}$$

The approach was to work out values for the equilibrium constant K_b from the conductivity data. Let the molality of the ions $[Me_2As\text{-}PPhMe_2^+] = [I^-] = [m]$ in the nitrobenzene solution.

Then:

$$K_b = \frac{[m]^2}{[Me_2AsI-m]\ [PhPMe_2-m]} \qquad \text{.........} \ I$$

To obtain values for $[m]$ conductivity data was required about an analogous salt which was totally ionised in nitrobenzene solution. For this purpose the results obtained from graph I of the molal conductance against $\sqrt{\text{molality}}$ for $Me_2As\text{-}P^+Et_3 \quad I^-$ were used. The assumption was made that $Me_2As\text{-}P^+Et_3 \quad I^-$ was totally ionised in solution, this was fairly reasonable in view of the cryoscopic measurements of its apparent molecular weight and the conductimetric titration result of Me_2AsI with Et_3P.

Thus from graph I:-

$$\Lambda_\infty = \Lambda + \alpha\sqrt{m} \qquad \text{.......... } 2$$

Λ = equivalent conductance in mhos.

Λ_∞ = equivalent conductance at infinite dilution in mhos.

m = molality of ions formed.

α = slope of graph of molal conductance against molality.

and it is known that:-

$$\Lambda = \frac{a}{R} \frac{1000}{m} \qquad \text{.......... } 3$$

combining 2 and 3

$$k = \frac{a}{R} = m\Lambda_\infty - \alpha m^{3/2} \qquad \text{.......... } 4$$

R = solution resistance in ohms.

a = cell constant.

$k = \frac{a}{R}$ = specific conductivity in mhos.

From graph I:-

$\Lambda_\infty = 42.57$ and $\alpha = 174$

from 4 $k = 42.57m - 174m^{3/2}$

From equation 4 values for $[m]$ were graphically obtained for the known values of k from the titration. On substitution of these values of $[m]$ in equation I it was found that the equilibrium constant K_b varied between infinity to unity. This was because some values of $[m]$ were greater than $[Me_2AsI]$. No data was available in order to take into account the activity coefficients of the charged ions when working out K_b.

The approach (b) was not rejected as the assumption that $Me_2As\text{-}P^+Et_3\ I^-$ was totally ionised in nitrobenzene solution had led to the values of $\Lambda_\infty = 42.57$ and $\alpha = 174$ being accepted for the case of $Me_2As\text{-}P^+PhMe_2\ I^-$. It was possible to find a value for K_b which was fairly constant by varying Λ_∞.

Although α is dependent upon Λ_∞, calculations were carried out where $\Lambda_\infty = 50, 55, 59$ and 60. These were done graphically and the results obtained for $[m]$ were once again substituted in equation 1 and values for K_b obtained. When $\Lambda_\infty = 50$, K_b diminished as $[Me_2AsI]$

increased; $\Lambda_\infty = 55$, K_b diminished as $[Me_2AsI]$ increased; $\Lambda_\infty = 60$, K_b increased as $[Me_2AsI]$ increased; and for $\Lambda_\infty = 59$, k was fairly constant.

The following table of results was worked out from the data obtained in the conductimetric titration of Me_2AsI with $PhPMe_2$ and using $k = 59m - 174m^{3/2}$.

k	m	Me_2AsI	$PhPMe_2$	$K_b = \frac{[m]^2}{[Me_2AsI-m]\,[PhPMe_2-m]}$
.1843	.0036	.0044	.02642	.71
.2855	.0062	.00838	.02515	.93
.3514	.00805	.01199	.02398	1.03
.3912	.00925	.01528	.02293	1.04
.4204	.01015	.01829	.02196	1.07
.4246	.0103	.0216	.02107	.92

In order to confirm that this approach was reasonable and fairly quantitative the results for the titration of Me_2AsI with C_5H_5N were examined by the same method; using $\Lambda_\infty = 59$, values for $[m]$ were found, and then the equilibrium constant K_b. For the titration of Me_2AsI with C_5H_5N:-

k	m	Me_2AsI	C_5H_5N	$K_b = \frac{[m]^2}{[Me_2AsI-m]\,[C_5H_5N-m]}$
.04734	.000875	.01204	.05933	.00117
.05972	.00112	.02309	.05688	.00103
.06760	.00128	.03322	.05461	.00095
.07348	.00140	.04262	.05252	.00093
.08086	.00155	.05939	.04879	.00088
.08622	.00166	.08049	.04409	.00082
.08989	.00174	.10303	.03907	.00095

Thus it can be seen from the two tables of results that values obtained for K_b are fairly constant. This interpretation confirms that the ions in solution are in equilibrium with the original reactants. The factor of about 1000 between the equilibrium constants can be regarded as a measure of the greater donor power of $PhPMe_2$ than C_5H_5N towards Me_2AsI.

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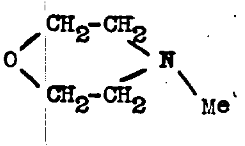
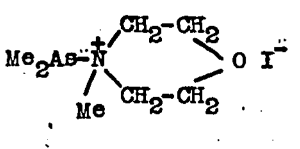
(M.Sc. Thesis, August 1960).

	PR_3	R_2MX	Salt	Solvent of crystallisation	m.p.^{e}	found			Analyses	
						C		H		C
1	PMe_3	Me_2AsI	$Me_2As{-}P^+Me_3\ I^-$	$EtOH/H_2O$	270-273°	20.2		5.1	$C_5H_{15}AsIP$	19.6
2	PEt_3	Me_2AsI	$Me_2As{-}P^+Et_3\ I^-$	EtOH	132-135	27.7		6.0	$C_8H_{21}AsIP$	27.6
3	PEt_3	Me_2AsBr	$Me_2As{-}P^+Et_3\ Br^-$	EtOH	142-145	31.8		7.1	$C_8H_{21}AsBrP$	31.8
4	PEt_3	Me_2AsCl	$Me_2As{-}P^+Et_3\ Cl^-$	$Et_2O/EtOH$	73-75	37.3		8.2	$C_8H_{21}AsClP$	37.2
5	PEt_3	$MeSbBr_2$	$Et_3P \longrightarrow SbMeBr_2$	EtOH	142-145 dec.	20.4	Br 39.1	4.2	$C_7H_{18}Br_2PSb$	20.3
6	PEt_3	Ph_2AsCl	white compound	MeOH	40-41	35.9	Cl 12.9	4.0	$C_{18}H_{25}AsClP$	51.4
7	PEt_3	Ph_2AsI	$Ph_2As{-}\overset{+}{P}Et_3\ I^-$	EtOH	85-87	45.4		5.6	$C_{18}H_{25}AsIP$	45.4
8	PEt_3	Ph2SbI,Cl	Not isolated							
9	PEt_3	Ph_2BiI,Cl	Not isolated							
10	PEt_3	Me_3SnBr	white compound	washed hexane	53-55	23.5		5.9	$C_9H_{24}BrPSn$	29.9
11	PEt_3	Et_3SnI,Cl	no reaction							
12	$PPr_3{}^n$	Me_2AsI	$Me_2As{-}P^+Pr_3{}^n\ I^-$	Pr^nOH	100	33.2		6.9	$C_{11}H_{27}AsIP$	33.7
13	$PPhMe_2$	Me_2AsI	$Me_2As{-}P^+PPhMe_2\ I$	EtOH	147	32.3		4.6	$C_{10}H_{17}AsIP$	32.4
14	$PPhMe_2$	Me_2AsBr	$Me_2As{-}P^+PhMe_2\ Br^-$	EtOH	178	38.3		5.6	$C_{10}H_{17}AsBrP$	37.3
15	$PPhMe_2$	Me_2AsCl	$Me_2As{-}P^+PhMe_2\ Cl^-$	Me_2CO	115-116	43.6		6.2	$C_{10}H_{17}AsClP$	43.3
16	$PPhMe_2$	Et_2AsI	$Et_2As{-}P^+PhMe_2\ I^-$	EtOH	112-118	36.4		5.5	$C_{12}H_{21}AsIP$	36.3
17	$PPhMe_2$	$MeSbBr_2$	$PhMe_2P \longrightarrow SbBr_2Me$	EtOH	175-176 dec.	24.9		3.1	$C_9H_{14}Br_2PSb$	24.9
18	$PPhMe_2$	Ph_2AsCl	white compound	Me_2CO	126	56.6	Cl 14.1	8.0	$C_{20}H_{21}AsClP$	59.8
19	$PPhMe_2$	Ph_2AsI	$Ph_2As{-}\overset{+}{P}PhMe_2\ I^-$	EtOH	107-108					
20	$PPhMe_2$	Ph_2SbI,Cl	Not isolated^9							
21	$PPhMe_2$	Ph_2BiI,Cl	Bi and $BiPh_3$ isolated							
23	$PPhMe_2$	Et_3SnI,Cl	No reaction							
24	$PPhEt_2$	Me_2AsBr	$Me_2As{-}P^+PhEt_2\ Br^-$	Pr^nOH	142-148	41.3		6.3	$C_{12}H_{21}AsBrP$	41.1
25	PPh_2Me	Me_2AsI	$Me_2As{-}P^+Ph_2Me\ I^-$	EtOH	115-117	42.1		4.5	$C_{15}H_{19}AsIP$	41.7
26	PPh_3	Me_2AsI	PPh_3 recovered 95%							
27	PPh_3	Me_2AsCl	PPh_3 recovered 91%							
28	C_5H_5N	Me_2AsI	$Me_2As{-}N^+C_5H_5\ I^-$	EtOH	194 dec.	28.6	I 39.0	3.3	$C_7H_{11}AsIN$	27.1
29	C_5H_5N	Me_3SnBr	$Me_3Sn{-}N^+C_5H_5\ Br^-$	washed hexane	64	29.8		4.8	$C_8H_{14}BrNSn$	28.9
30	$(C_5H_4N)_2$	Me_2AsI	white compound	would not crystallise			no analysis			
31	$(C_5H_4N)_2$	Me_3SnBr	not isolated							
32		Me_2AsI		EtOH	113	25.3		5.1	$C_7H_{17}AsINO$	26.2

a. The conductimetric titration results were worked out graphically, curved graphs were obtained at the end point. See graphs III, IV and V.

b. The considerable curve at the end point also indicated that a 1 C_5H_5N:2 Me_2AsI compound could exist. See graph V.

c. The conductimetric titration results showed an increase in conductivity indicating salt formation. The graphs were very curved and no equivalent ratios could be obtained from them.

d. A solution of $Et_3P \longrightarrow SbMeBr_2$ in nitrobenzene had a low conductance. The bromine present was not ionic as silver bromide was slowly precipitated from an aqueous acetone solution of the compound by silver nitrate.

e. The melting points obtained were the results of using a stem corrected thermometer. The salt crystals softened at the lower quoted temperature range and then melted. The melt usually slowly decomposed and distilled off.