Reactions of some unsaturated compounds with organic and hydride derivatives of group III elements

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REACTIONS OF SOME
UNSATURATED COMPOUNDS WITH ORGANIC AND
HYDRIDE DERIVATIVES
OF
GROUP III ELEMENTS

by

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MEMORANDUM

The work included in this thesis was carried out at the Science Laboratories of the University of Durham between September 1963 and May 1966, and has not been submitted for any other degree. Part of this work has already been the subject of a publication in the Journal of the Chemical Society. All the work described is the original work of the author, except that acknowledged by reference.

SUMMARY

Hydroboration reactions of methyl cyanide have been studied. The reaction of diborane with methyl cyanide proved a convenient preparative route to N-triethylborazine, $Et_3N_3B_3H_3$, and in this reaction, small quantities of N-diethylaminodiborane are formed. Reactions between mixed chloroboranes, $HBCl_2$ and H_2BCl, and methyl cyanide proceed via a disproportionation into methyl cyanide-boron trichloride adduct, $MeCNBCl_3$, and a mixture of partially chlorinated N-triethyl borazines $Et_3N_3B_3H_nCl_{3-n}$.

Adducts Bu^tCN,AlR'_3 (R' = Me, Et, or Ph), $Bu^tCN,AlMe_2Cl$, have been prepared and their rearrangement at 150-240° to the dimeric alkylideneamino derivatives $(RR'C{:}NAlR'_2)_2$ studied. Dimethylaluminium hydride with Bu^tCN gives $(Bu^tCH{:}NAlMe_2)_2$ directly. The electronic and steric factors that appear to influence these rearrangements and the reactivity of the product are noted, and interpreted in terms of possible mechanisms. Features of the infrared spectra of these compounds are discussed, and the proton nuclear magnetic resonance spectra of many of the alkylidene amino-compounds are interpreted as evidence for trans-structures.

Adducts RCN,GaR'_3 (R = Me,Ph and Bu^t, R' = Me and Et) have been prepared and their thermal decomposition reactions studied. Methyl 'migration' was not observed, and the only rearrangement reactions to go involved the evolution of ethylene with subsequent migration of hydrogen from the triethylgallium adducts. Features of the infrared and nuclear magnetic resonance spectraare discussed.

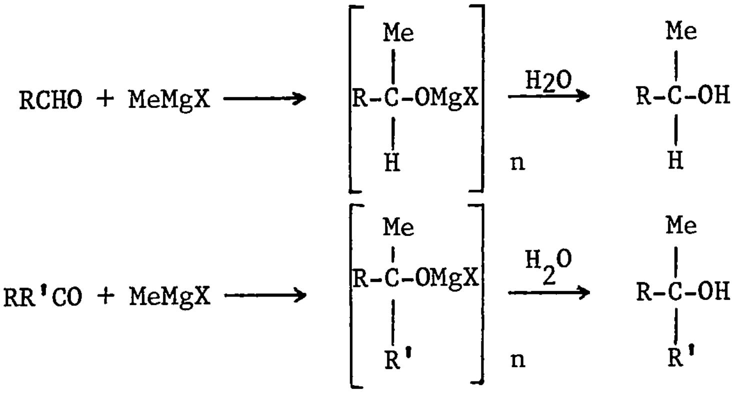
Acetoxime reacts at *ca.* 100° with trimethylborane to form methane and the isopropylideneaminoxy derivative $(Me_2C:NOBMe_2)_2$ which apparently exists as dimeric units in the crystal phase, is partly associated in solution, and as a monomer in the gas phase. Trimethyl-aluminium, -gallium, and -indium react with acetoxime at -78 to form related compounds $(Me_2C:NOMMe_2)_2$ (M = Al, Ga, or In), considered to be dimeric in the gas, solution and crystal phases. Trimethylthallium at room temperature gives the formally analogous $(Me_2TlON:CMe_2)$ for which spectroscopic evidence indicates possibly a different structure. Assignments are suggested for characteristic bands in the infrared spectra of these compounds, and their proton magnetic resonance spectra, which show an unusual solvent effect are recorded. The mass spectra of the boron and aluminium compounds are consistent with the proposed structures.

Introduction

In recent years, many workers have been investigating the addition reaction whereby a dipolar group M-X adds across a multiple bond A=B.

$$\text{i.e. } \overset{\delta+}{M} - \overset{\delta-}{X} + \overset{\delta-}{A} = \overset{\delta+}{B} \longrightarrow \text{M-A-B-X.}$$

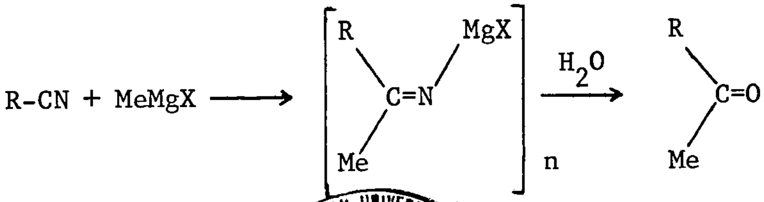
One of the first reactions of this type to be discovered was that of diethylzinc with acetaldehyde[1] by Wagner in 1876, and more recently, in 1900, Victor Grignard[2] published the first description of some of the properties and reactions of ethereal solutions of alkyl or aryl magnesium halides, (later to be known as Grignard reagents), with multiply bonded functional groups. Since then it has been found that M can be almost any relatively electropositive element and X can be almost any comparatively electronegative element or group. Reactions of this type have proved very useful in synthesis, and examples may be drawn from the reactions of Grignard reagents[3], to form alcohols from aldehydes and ketones,



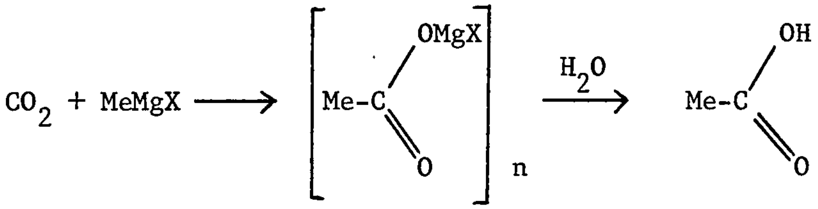
$$\text{RCHO} + \text{MeMgX} \longrightarrow \left[\text{R-}\overset{\text{Me}}{\underset{\text{H}}{\text{C}}}\text{-OMgX}\right]_n \xrightarrow{H_2O} \text{R-}\overset{\text{Me}}{\underset{\text{H}}{\text{C}}}\text{-OH}$$

$$\text{RR'CO} + \text{MeMgX} \longrightarrow \left[\text{R-}\overset{\text{Me}}{\underset{\text{R'}}{\text{C}}}\text{-OMgX}\right]_n \xrightarrow{H_2O} \text{R-}\overset{\text{Me}}{\underset{\text{R'}}{\text{C}}}\text{-OH}$$

ketones from nitriles,



and carboxylic acids by carbonation.



$$CO_2 + MeMgX \longrightarrow [Me\text{-}C(=O)OMgX]_n \xrightarrow{H_2O} Me\text{-}C(=O)OH$$

The literature on this subject is vast and is best summarised in tabular form (See tables I to IV). These collect together information available on reactivities of a range of derivatives M-X of elements of groups 2,3 and 4 of the periodic table towards unsaturated systems.

Since reactivities of unsaturated groups towards a particular group MX increases in the sequence

$$RC{\equiv}N < R_2CO < RNCO$$

Groups MX themselves can be classified according to their reactivities as follows:

A Very reactive - Reacts with cyanides and olefins, etc.

B Moderately reactive - Reacts with ketones, etc.

C Slightly reactive - Reacts only with very reactive groups such as isocyanate and other A=B=C systems.

D Does not show any addition reactions.

"?" denotes that the work has not been done, and other figures are reference numbers.

Too much reliance should not be placed on the relative reactivities of the group M-X because particularly in the cases where X is OR, SR, NR_2, the full range of unsaturated groups A=B, from cyanide to isocyanate, has not been fully studied.

Table I

	M = Beryllium	Magnesium	Calcium
X = H	A 4	A 6	?
Alkyl	A 5	A 3	?
Aryl	?	A 3	B 8
Amino	?	A 7	?
Alkoxy	?	?	?
Thioalkoxy	?	?	?
Phosphino	?	?	?

Table II

	M = Zinc	Cadmium	Mercury
X = H	B122	?	-
Alkyl	C122	C120	D
Aryl	B122	?	D
Amino	C119	?	(?)
Alkoxy	C119	?	C121
Thioalkoxy	?	?	?
Phosphino	?	?	?

Table III

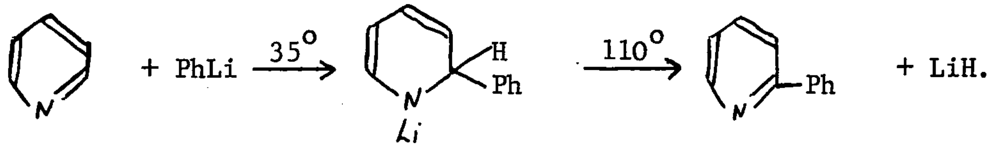
	M = Boron	Aluminium	Gallium
X = H	A 9	A 14	A 17
Alkyl	C 10	A 15	B 17
Aryl	C 11	A 16	?
Amino	C 12	?	?
Alkoxy	C 12	?	?
Thioalkoxy	C 13	?	?
Phosphino	?	?	?

Table IV[*]

	Silicon	Germanium	Tin[25]
H	A 53	B 19	B 21
Alkyl	D	D	D
Aryl	D	D	D
Amino	C 18	C 20	C 22
Alkoxy	C 18	?	B 23, 24
Thioxy	?	?	?
Phosphino	?	?	?

[*] Some reactions go by a free radical mechanism.

The alkyls and aryls of lithium have been much used in organic synthesis. They are chemically similar to, but more reactive than Grignard reagents, as is shown by their reaction with pyridine



The organo-derivatives of sodium and the heavier alkali metals are extremely reactive, due to the presence of a carbanion, and combine with nearly all substances except nitrogen, the inert gases and the paraffin hydrocarbons. Alkyl sodium compounds even react with benzene, giving an anion which has a maximum delocalisation of charge.

$$\overset{-}{Bu}\overset{+}{Na} + C_6H_6 \longrightarrow \text{Butane} + (C_6H_5)^-Na^+$$

In the present work, an investigation has been made of the reactions between unsaturated compounds, mainly nitriles, and organo-, and hydrido compounds of Group III elements.

In the following pages, a brief review is made of reactions in which compounds of boron aluminium and gallium are known to add to multiply bonded systems.

Reactions of Boron compounds with unsaturated compounds

Hydroboration

The term hydroboration describes the reaction in which a boron hydride or boron hydride derivative adds across a multiple bond.

This reaction has been much studied, and is the subject of a book by H. C. Brown.[9] Prior to 1956, the only hydroboration reactions known were those of diborane with one or two unsaturated hydrocarbons, yielding organo-boron compounds.[26] Conditions were inconvenient, and yields were poor. In 1956, Brown and his co-workers discovered that when ethers and other weak bases were used as solvent, these greatly catalysed the addition of the boron-hydrogen group across the multiple bond.[27] Since then, hydroboration has become a much valued reaction in organic synthesis.

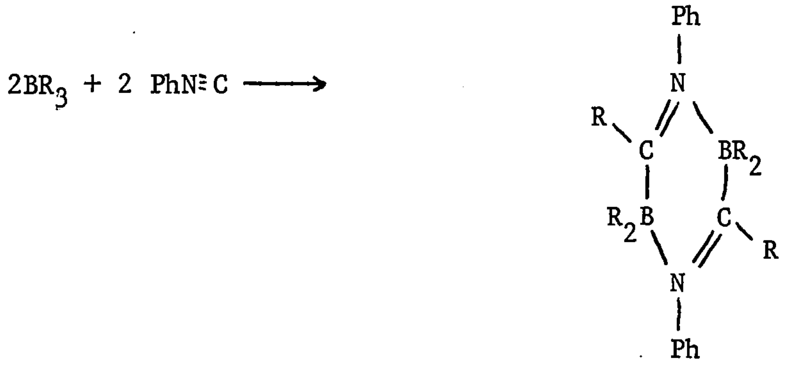
The reaction of diborane with olefins is a convenient method for the preparation of organoboron compounds. This addition reaction is highly stereo specific, and generally, the boron becomes attached to the less substituted and therefore more negative carbon atom of the double bond.[28] Also, the addition of B-H bonds to terminal olefins is faster than addition to non-terminal olefins, and treatment of a mixture of 1- and 2-pentene with a deficiency of diborane results in the selective conversion of the terminal olefin into tri-n-pentylboron.[29]

$$6\text{n-PrCH=CH}_2 + \text{B}_2\text{H}_6 \longrightarrow 2(\text{nC}_5\text{H}_{11})_3\text{B}$$

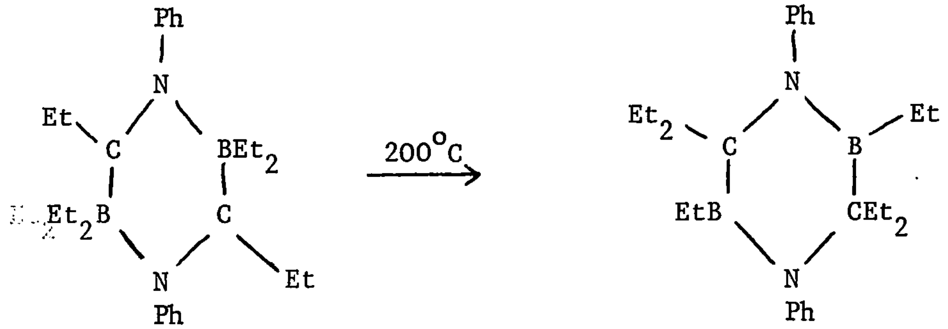
Reactions of organoboranes with alkaline hydrogen peroxide yield alcohols, and this becomes a valuable method for the 'anti-Markovnikov' formation of alcohols from olefins.

Organoboration

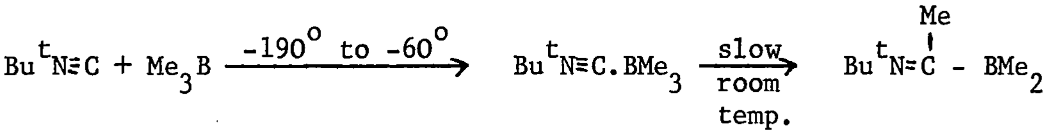
Organic groups bound to boron are much less reactive than hydrogen, due to the similarity of the electronegativities of boron and carbon, and organo-boration reactions are only observed with the more reactive multiply bonded systems. Trimethyl- and triethylboron do not react with methyl cyanide,[30] but isocyanides form adducts at low temperature which rearrange slowly at room temperature to give azomethine derivatives.[31]



When R is ethyl, the compound rearranges further into a 2•5 diboropiperazine above 200°C.



When t-butyl isocyanide reacts with trimethylboron, the rearranged product is monomeric, and apparently thermally stable, since transfer of a second methyl group is not reported.[32]

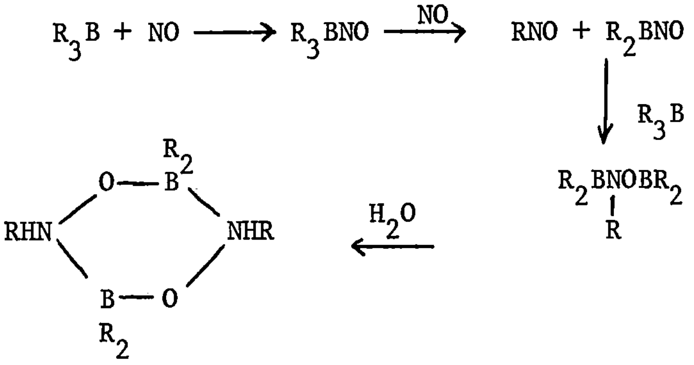


$$\mathrm{Bu^tN{\equiv}C} + \mathrm{Me_3B} \xrightarrow{-190^\circ\ \text{to}\ -60^\circ} \mathrm{Bu^tN{\equiv}C.BMe_3} \xrightarrow[\text{room temp.}]{\text{slow}} \mathrm{Bu^tN{=}\overset{Me}{\overset{|}{C}} - BMe_2}$$

Organoboron compounds also react with oxygen to yield thermally stable organoboron peroxides, which rearrange at room temperature to the alkoxides,[33]

$$\mathrm{Me_3B + O_2 \longrightarrow Me_2\ BOOMe \longrightarrow MeB(OMe)_2}$$

Reaction with nitric oxide yields on hydrolysis a boron, oxygen-nitrogen heterocyclic compound.[34] (BON-BON derivative)



Chloroboration, aminoboration and alkoxyboration

A lot of work has been published recently, by Lappert and his co-workers about the reactions of boron halides, amides and alkoxides with acetylenes,[11] isocyanates,[11,12] etc., and carbodi-imides.[35] These are all relatively reactive systems and it is difficult to assess the absolute reactivity of the boron compound because work on less reactive bonded systems has still to be done. The relative migratory aptitudes of the groups bound to boron have been determined by studying the reactions of 'mixed' boron compounds, e.g. $\mathrm{MeOBCl_2}$, $\mathrm{PhBCl_2}$ etc., with p-tolylcarbodiimide.[35] The following order has been found:

(a) $NHR > NR_2 > SR > Ph > Cl$.

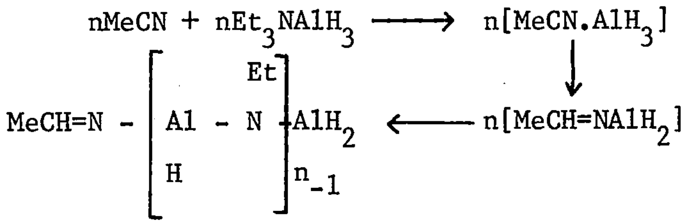
(b) $OR > Ph$.

(c) $Cl > OR$.

This implies that the more reactive derivatives such as the aminoboranes may react with ketones and possibly even with the more reactive cyanides.

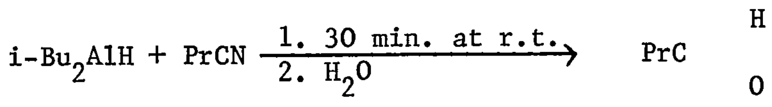
Reactions of Aluminium compounds with Unsaturated Compounds.

Aluminium hydride and its derivatives are much more reactive than their boron counterparts. Aluminium hydride-triethylamine complex reacts rapidly at room temperature with acetonitrile,[36] forming aluminium-nitrogen polymers,



$$\begin{aligned} &nMeCN + nEt_3NAlH_3 \longrightarrow n[MeCN.AlH_3] \\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ &MeCH{=}N-\left[\overset{}{\underset{H}{Al}}-\overset{Et}{N}\right]_{n-1}AlH_2 \longleftarrow n[MeCH{=}NAlH_2] \end{aligned}$$

but trimethylamine borane can be recovered quantitatively from an equimolar mixture with acetonitrile, after standing for a period of several weeks.[37] Alkylaluminium hydrides react at or below room temperature with cyanides,[14,38], with the formation of azomethine derivatives. The reaction of di-isobutylaluminium with various cyanides in ether, benzene or heptane is a synthesis for aldehydes.



$$i\text{-}Bu_2AlH + PrCN \xrightarrow[2.\ H_2O]{1.\ 30\ min.\ at\ r.t.} PrC\overset{H}{\underset{O}{}}$$

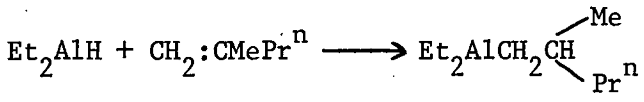
Direct distillation of a mixture of propyl cyanide and di-isobutylaluminium hydride gives n-butylideneaminodi-isobutylaluminium.

$$\mathrm{PrCN + i\text{-}Bu_2AlH \longrightarrow (PrCH{:}NAlBu^{i}_{2})n.}$$

Alkylaluminium hydrides react smoothly with olefins.[39] Secondary olefins react with Al-H bonds about one hundredth as rapidly as primary olefins, and as in hydroboration, the hydrogen atom becomes attached to the more substituted carbon atom of the olefin:

$$\mathrm{CH_3\overset{\delta+}{CH} = \overset{\delta-}{CH_2} + \overset{\delta-}{H} - \overset{\delta+}{Al}\!<\ \longrightarrow CH_3CH_2CH_2Al\!<}$$

Mixed trialkyls of aluminium have been prepared from dialkylaluminium hydride and olefins:



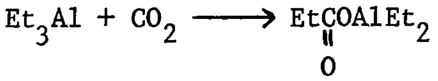
$$\mathrm{Et_2AlH + CH_2{:}CMePr^n \longrightarrow Et_2AlCH_2CH(Me)Pr^n}$$

though mixed aluminium alkyls are liable to disproportionate. Variations[40] on this reaction have been used extensively for the preparation of hydrocarbon polymers, and of organoaluminium compounds with a known number of carbon atoms in the hydrocarbon chain, oxidation followed by hydrolysis of which yield long chain primary alcohols, much in demand by the detergent industry.

Lithium aluminium hydride is a more experimentally convenient material to handle, and has been extensively used for the reduction of unsaturated Compounds.[41] It is rather soluble in ether and is conveniently used as an ethereal solution, but the more common procedure is to add the substance to be reduced to a slurry of the hydride in diethyl ether, tetrahydrofuran or di-n-butyl ether. It is much more reactive than alkyl aluminium hydrides since the reaction product is usually a derivative of the lowest reduced state of the functional group, e.g. benzonitrile and o-toluonitrile[42] can be reduced to the corresponding amine in 80% yield whereas the reaction of phenyl cyanide with dimethylaluminium hydride stops at the azomethine stage.[38]

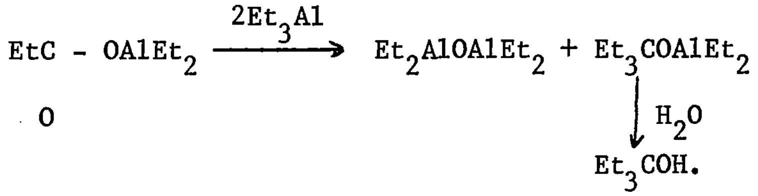
The reason for this marked difference in reactivities is probably that the hydrogen in the tetrahydroaluminate anion AlH_4^- has more negative character than the hydride in dimethylaluminium hydride, due partly to the negative charge on the anion and also due to the aluminium-hydrogen-aluminium three-center bonds in the associated alkyl aluminium hydrides.

Aluminium trialkyls, though less reactive than their hydride counterparts also react by addition of R-Al across the multiple bond with a wide range of multiply bonded systems. The reactions of aluminium alkyls with with olefins and acetylenes has been described in some detail by K. Ziegler[40] and so will not be further discussed here. The lower alkyls take fire in oxygen, but the reaction can be controlled with the formation of aluminium alkoxides.[43, 44, 45.] Triethylaluminium[43, 46] reacts readily with carbon dioxide, with the formation of Diethylaluminium propionate.



$$Et_3Al + CO_2 \longrightarrow Et\underset{\underset{O}{\|}}{C}OAlEt_2$$

When an excess of triethylaluminium is used, a multi-stage reaction occurs, with the formation of an alkoxide

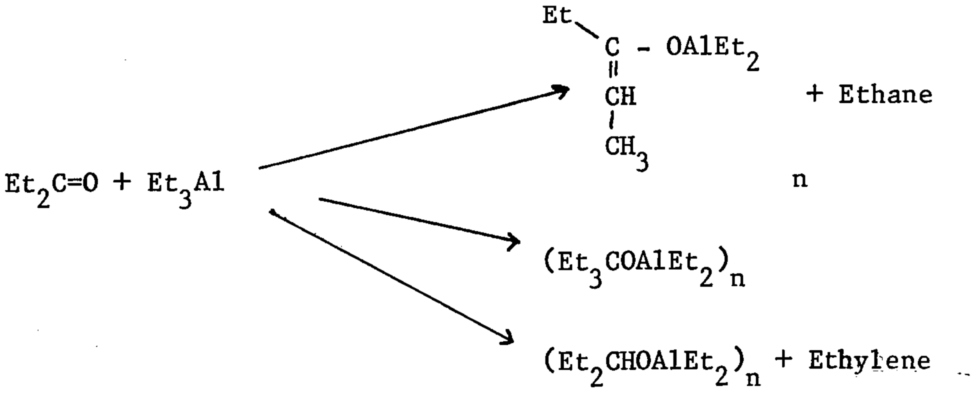


$$\underset{\textstyle O}{EtC} - OAlEt_2 \xrightarrow{2Et_3Al} Et_2AlOAlEt_2 + Et_3COAlEt_2 \xrightarrow{H_2O} Et_3COH.$$

Aluminium alkyls, like Grignard reagents, add to <u>aldehydes</u> and <u>ketones</u> with the postulated formation of an intermediate alkoxide, hydrolysis of which yields alcohols.

$$Ph_2C{=}O + Me_3Al \longrightarrow (Ph_2MeCOAlMe_2)n$$

When acidic ketones, i.e. those that show keto-enol tautomerism, are used, alkane evolution may become a side reaction, and the extent to which alkane evolution is observed is a reflection of the enolic character of the ketone. When somewhat branched chain aluminium alkyls are used, olefin evolution from the alkyl groups and hydrogen transfer may become the side reaction.



This tendency is inhibited by use of an excess of the organometallic compound.[47]

$$Et_2C{=}O + \text{excess } Et_3Al \longrightarrow (Et_3COAlEt_2)_n.$$

Adkins and Scanby[48] have found that alkyl aluminium chlorides react with acid chlorides to give ketones.

$$R'_2AlCl + RCOCl \longrightarrow RAlCl_2 + R'COR$$

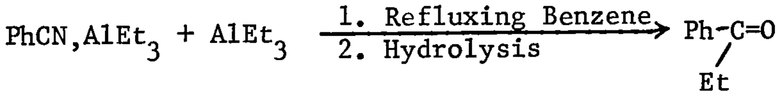
Aluminium trialkyls cannot be used for a smooth ketone synthesis because the first aluminium-carbon bond is too reactive. The whole process would thus be complicated by the additional reaction between free aluminium alkyl and ketone. Alkylaluminium dichlorides also react with acid chlorides to give ketones.

$$RAlCl_2 + R'COCl \longrightarrow RR'C{:}O + AlCl_3.$$

Unlike the previous reactions, aluminium alkyls only add across the C N of a cyanide at elevated temperatures. A sample of phenyl cyanide-trimethylaluminium adduct,[38] $PhC{\equiv}N,AlMe_3$, only rearranges at 160-170°C. Unless excess organoaluminium compound is used, methyl- is the only alkyl group which will add across a cyanide;[16] other alkyl groups lose olefin and hydride transfer occurs.

$$PhCN,AlMe_3 \xrightarrow{165^o} (PhMeC{=}NAlMe_2)_2 \quad (38)$$

$$PhCN,AlEt_3 \xrightarrow{165^o} (PhHC{=}NAlEt_2)_2 + C_2H_4 \quad (38)$$



$$PhCN,AlEt_3 + AlEt_3 \xrightarrow[\text{2. Hydrolysis}]{\text{1. Refluxing Benzene}} \underset{\displaystyle Et}{Ph{-}C{=}O} \quad (14)$$

Aluminium alkyls also react with sulphur dioxide[46], dinitrogen tetroxide[49], and isocyanates[14] etc.

The addition reactions of arylaluminium compounds are similar to those of the trialkyls, but tend to occur less readily, and in some cases are more complicated. The aryls have been shown to react with carbon dioxide[50], aldehydes and ketones,[51] phenyl cyanide,[52,38] and phenyl isocyanate.[50]

Reactions of other Group III alkyls with Unsaturated Compounds

Only trimethylgallium has had any attention in this field. Trimethylgallium[53] forms a weak coordination complex with methyl cyanide, but this is completely dissociated at 100°C, and no addition of the gallium-methyl across the C N of the cyanide was observed at this temperature. Gentle pyrolysis of a mixture of acetone and trimethylgallium gave quantitative methane evolution, with no tertiary butanol produced on hydrolysis. No attempted addition reactions of indium and thallium alkyls appear to have been reported.

Experimental Methods and Techniques

Nitrogen Supply

"White-spot" quality nitrogen available on the benches was purified by passage through a furnace containing reduced wire-form copper at ca. 400°C and then through two traps at -196°C. Periodically, the copper was regenerated with hydrogen.

Glove Box

Samples of involatile compounds for analysis, infrared spectra and nuclear magnetic resonance spectra were made up under nitrogen in a glove box of the conventional type. The nitrogen was purified as described above, and the nitrogen inside the glove box was continuously recycled through the purification system by a small pump fitted inside the box. Copper piping was used outside the box, to avoid the difficulty caused by the permeability of oxygen to P.V.C. tubing.

Vacuum System

A vacuum system (Photograph 1) was constructed for the manipulation of many of the volatile compounds used in this investigation. It consisted essentially of three parts: (a) a storage section, (b) a fractionation section, and (c) a gas measurement section.

The storage section consisted of 3-l bulbs which were used for compounds gaseous at room temperature such as diborane and dimethylamine,

PHOTOGRAPH I

and several "cold fingers" which could contain up to 30-ml. of compound. These were used for the storage of less volatile air-sensitive compounds, e.g. trimethylgallium.

The fractionation section consisted of four straight-limbed U-traps which were both interconnected, and independently connected to the main manifold by mercury float valves.

The gas measurement section was constructed in two sections. A Topler pump was used to pump non-condensable gases into a calibrated bulb, and pressures were measured relative to a manometer beside the bulb. The bulb was calibrated by weighing the quantity of mercury needed to fill it to an etched mark. The section for condensable gases consisted of a 3-litre bulb and cold finger joined by a mercury float valve to a 500-ml. bulb and cold finger. A single limb manometer was connected to the smaller section so that the gas could either be measured in the smaller bulb alone, or in the combined section. The bulbs were calibrated by condensing in known amounts of carbon dioxide. The carbon dioxide was measured in a bulb which had been calibrated by weighing the quantity of water needed to fill it.

<u>Calibrations for the measurement section</u>

Volume of small Topler bulb = 13·62 c.c.
Volume of combined Topler bulbs = 149·4 c.c.
Volume of small standard bulb = 684·95 c.c.
Volume of combined standard bulbs = 4357·7 c.c.
Internal diameter of the manometer = 10 mm.
For 1 cm. drop on manometer, increase in volume = 0·786 ccs.
For 1 cm. drop on manometer, rise in reservoir = 0·0368 cm.

A rotary oil pump backing a mercury diffusion pump was used for evacuating the system. A second rotary oil pump was used for operation of the mercury float valves and the Topler pump.

Construction throughout used exclusively mercury float valves, except at the inlets, and at the pumps, where large-bore greased taps were used to isolate the pumps from each other and from a liquid air trap used to prevent volatile materials from going into the rotary oil pump.

Infrared Spectra

Infrared spectra (range 2 to 25 microns) were recorded either on a Grubb-Parsons GS2A prism-grating spectrophotometer or Spectromaster; spectra in the range 21-50 microns were recorded on a Grubb-Parsons DB3/DM2 caesium iodide spectrophotometer. Samples of involatile materials were in the form of nujol mulls, liquid films or cyclohexane solutions. Gases were recorded using a 10 cm. potassium bromide cell. Vapour-phase spectra of only slightly volatile compounds were obtained using a Perkin-Elmer heated gas cell with potassium bromide windows.

Nuclear Magnetic Resonance Spectra

Proton magnetic resonance spectra were recorded at 60 Mc./sec. on an A.E.I. RS2 or a Perkin-Elmer R10 spectrometer. Samples were either pure liquids or solutions in carbon tetrachloride, benzene, cyclohexane, deuteromethylcyclohexane or deutero-toluene. Tetramethylsilane was commonly used as the reference compound, but on occasions it was necessary to use either benzene or cyclohexane.

Boron (^{11}B) nuclear magnetic resonance spectra were recorded at 19·75 Mc./sec. on a Perkin-Elmer R10 spectrometer. Samples were in the form of approximately 10% toluene solutions, with trimethyl borate as an external reference.

Analytical Methods

Carbon and Hydrogen Analysis

Carbon and hydrogen analyses were carried out by combustion, by the departmental analytical group directed by Mr. T. Holmes. Carbon and hydrogen analysis on boron compounds were carried out by external professional analysts. (Dr. Weiler and Dr. Strauss, Oxford).

Hydrolyses

Organic groups attached to aluminium, and hydrogen attached to boron or aluminium, were determined by hydrolysis and measurement of the hydrocarbon or hydrogen evolved. Volatile compounds were condensed into a flask, weighed and then transferred on the vacuum line to another flask in which they were subsequently hydrolysed. Involatile compounds were either transferred in the glove-box, or, on the bench, under nitrogen. The compounds were hydrolysed with a few c.c. of de-aerated 2-methoxy ethanol followed by dilute sulphuric acid. The bases evolved were passed through a trap to remove any 2-methoxyethanol, and measured using the Topler pump.

Aluminium Analysis

The aluminium content of a compound was determined by the E.D.T.A. method.[55]

The whole of the solution left after hydrolysing a sample containing about 0•020 gm. of aluminium was placed in a large conical flask. The solution was evaporated almost to dryness, and concentrated nitric acid was added to destroy any organic matter. The solution was evaporated almost to dryness, and the resulting white solid was dissolved in a minimal amount of dilute sulphuric acid. If organic matter still remained after the nitric acid treatment (which was often the case with phenylaluminium compounds), perchloric acid was added, and the evaporation procedure repeated. The sulphuric acid solution was made up to 500 ml. with distilled water.

A 50 ml. aliquot of this was taken, and titrated with approximately 0•2 N caustic soda, with B•D•H• 4•5 indicator, the end-point being a pale grey colour. A further 50 ml. aliquot was taken and the determined amount of the caustic soda solution was added. Then 10 ml., an excess, of 0•01m. EDTA. solution, a drop of Xylenol Orange solution and a few crystals of hexamine were added. The solution was warmed to 35°C and titrated with 0•01m. zinc acetate solution. The end-point was a sharp change from pale pink to a straw yellow.

Gallium and Indium Analysis

Organo- gallium and -indium compounds are not completely hydrolysed by dilute acids. Their derivatives were boiled for several hours with concentrated hydrochloric acid to effect complete cleavage of alkyl groups. The resulting solution was evaporated almost to dryness, concentrated nitric acid was added, and from this point, the procedure followed was that used for aluminium determination.

Thallium and Lithium Analysis

The thallium and lithium compounds prepared were rapidly hydrolysed by water into dimethylthallium hydroxide and lithium hydroxide respectively. These are strong bases, and were consequently titrated with 0•10 N sulphuric acid.

Boron Analysis

The sample was burned in an apparatus described and illustrated in a Ph.D. thesis in 1963 by Dr. J. Graham of this laboratory.

The compound was weighed in a small gelatine capsule filled in the glove box. The amount used was up to 0•1 gm. A large (3 litre) dropping funnel was purged with oxygen, and 50 c.c. water placed in it. The gelatine capsule was placed in a platinum gauge container attached to the stopper of the dropping funnel. A small piece of filter paper was used as a fuse. This was lit and the stopper was quickly placed in the dropping funnel. After a few seconds, the compound burned with a bright green flame. When the combustion was complete, the dropping funnel was shaken to dissolve the combustion products. The contents were then rinsed into a flask, made up to a standard volume and titrated against standard 0•1 N caustic soda in the presence of mannitol with bromothymol blue as indicator.

Molecular Weights

Molecular weights were determined cryoscopically in benzene. Analytical grade benzene was dried over sodium wire and was calibrated with biphenyl. A Beckmann apparatus of conventional type was used, and all measurements were taken while a slow stream of nitrogen was passed through the apparatus. The optimum freezing point depression was $0{\cdot}15^{o}$ and the solution was allowed to supercool to $0{\cdot}1^{o}$ below the true freezing point.

Vapour phase molecular weights of very volatile compounds were measured by filling a calibrated bulb to a known pressure at room temperature, and weighing the compound in the bulb.

Vapour phase molecular weights of less volatile compounds were measured using a high-temperature bulb attached to the vacuum system. This consisted of a bulb of known volume which could be closed off by a mercury U-tube, which also acted as a manometer. The whole apparatus was immersed in a five litre bath of oil which was heated electrically. Known weights of compound were condensed into the bulb, which was heated to about 20^{o} above the temperature at which all the compound was in the vapour phase. Corrections were made for the changing density and vapour pressure of the mercury in the manometer which became significant at temperatures in excess of $100^{o}C$.

Preparation of Starting Materials

Dimethylmercury. b.p. 92°C.

This was prepared by the reaction of mercury (II) chloride with methylmagnesium bromide.[56]

Magnesium turnings (125 g.) and dry ether (1•5 l.) were placed in a five-litre three necked flask, which had been previously purged with pure nitrogen. The flask was fitted with a stirrer, a pressure-equilibrated dropping funnel and a cold-finger condenser, maintained at -78°C by an acetone/carbon dioxide mixture. The dropping funnel was cooled by surrounding it with crushed solid carbon dioxide and was filled with a solution of methyl bromide (500 gm.) in ether (500 c.c.). The reaction was initiated with 0•25 c.c. of ethylene dibromide, and the methyl bromide added at such a rate that the solution refluxed gently. When addition was complete, the mixture was allowed to reflux for a further hour.

The cold finger was replaced by a sintered-disc Soxhlet extractor with a water condenser fitted at the top. Mercury (II) chloride (490 gm.) was placed on the sintered disc, and was extracted into the Grignard reagent by refluxing the mixture, until extraction was complete. The mixture was hydrolysed with water, and the precipitated magnesium salts were dissolved by the addition of concentrated hydrochloric acid. The ether layer was separated and the aqueous layer extracted with two 500 ml. portions of ether. The combined ether extracts were dried by standing over anhydrous magnesium sulphate, and the bulk of the ether was distilled off through a long fractionating column, filled with Fenske helices. When the pieces of porous pot began to float, the fractionating column was replaced by a smaller one, and after removal of the remaining ether, the dimethylmercury was distilled as a colourless liquid. A total of 273 gms. of dimethylmercury was obtained (70% yield).

Trimethylgallium. b.p. 56°C.

Trimethylgallium was prepared by the exchange reaction between gallium metal and dimethylmercury.[57] The reaction was carried out in an all-glass apparatus, which consisted of a 250 c.c. flask to which was attached an efficient fractionating column, and a constricted side-arm. A side-arm at the top of the column led to a 'cold-finger' and a mercury cut-off, which could be raised or lowered to take off some trimethylgallium from the top of the column. The apparatus was evacuated as far as possible and was then filled with pure nitrogen. All reactants were introduced into the apparatus against a counter-current of nitrogen.

Gallium metal (25 gm.) which had been previously washed from traces of grease with boiling benzene, and mercury (II) chloride (0·1 gm.) were placed in the reaction flask and dimethylmercury (123·8 gm.) was added by syringe through the constricted side-arm. The flask and contents were cooled in liquid air, and the side-arm sealed off. The reaction mixture was heated and dimethylmercury refluxed. After 36 hours, the temperature at the top of the column began to drop and eventually reached 56°C. Fractions boiling between 55·5°C and 56·5°C were removed periodically until the reaction had gone to completion. The trimethylgallium was distilled onto the vacuum line for storage and no further fractionation was found to be necessary. The yield of trimethylgallium was 37 gm., corresponding to a yield of 90% based on the amount of gallium metal used.

Triethylgallium. b.p. 142•6°C

Triethylgallium was prepared by the exchange reaction between gallium metal and diethylmercury[58] and by the reaction of triethylaluminium with gallium chloride.[59]

(a) The reaction between gallium and diethylmercury was carried out in an evacuated sealed tube, fitted with a fragile tipped side-arm. Gallium metal (7•8 gm.), washed free from traces of grease by boiling benzene, was placed in the tube, and diethylmercury (43 gms.) was added by syringe. The tube was then attached to the vacuum line, cooled in liquid air, pumped out, and then sealed off. The tube was then placed in an oven at 170°C for 4 days, and was subsequently opened, and the triethylgallium distilled onto the vacuum line where it was stored. No further purification was necessary. The yield was 16•6 g. 95% of theory.

(b) Gallium chloride (15 g.) and dry hexane (50 ml.) were placed in a 250 c.c. three necked flask, fitted with a stirrer and a condenser. Triethylaluminium (30 g.), was slowly added by syringe, against a counter current of pure dry nitrogen, and the mixture was then maintained at 70° for three hours. The hexane was distilled off through a short column at atmosphere pressure, and the triethylgallium was removed by distillation at reduced pressure. The product was finally purified by a fractional distillation at atmospheric pressure. The yield of triethylgallium was 8•5 g., 66% of theory.

Dimethylaluminium hydride

This was prepared by the reaction of lithium aluminium hydride with trimethylaluminium.[60]

A thick-walled Pyrex tube with a fragile tipped side-arm and a constricted neck was prepared, and was filled with pure dry nitrogen. Lithium aluminium hydride (20 g.), dry cyclohexane (100 ml.) and trimethylaluminium (20 g.) were introduced into the tube against a counter flow of nitrogen. The tube and contents were attached to the vacuum line, frozen down in liquid air, evacuated, and the tube was sealed off at the constriction. The reaction mixture was maintained at 70°C for 24 hours. The tube was then opened and the cyclohexane and dimethylaluminium hydride distilled off, under vacuum, into a two-necked storage flask. The pure hydride is a very viscous, highly reactive and only slightly volatile liquid and is thus most conveniently stored as a cyclohexane solution. The concentration of the solution was determined by hydrolysing a known volume of solution and measuring the mixture of methane and hydrogen evolved.

The yield of product was 14 g., 85% of the quantity expected from the amount of trimethyl-aluminium used.

Diborane

Diborane was prepared by several methods, and the best preparation was by the reaction of lithium aluminium hydride with boron trifluoride ether.[61] complexes.

The apparatus consisted of a three necked complex one-litre flask, fitted with a pressure-equilibrated dropping funnel, a stirrer, and a "cold-finger" condenser maintained at -78°C. The outlet of the condenser was connected to three traps, the first of which was cooled to -78°C. by an acetone/carbon dioxide slush bath, and the others were cooled in liquid air. The whole apparatus was purged out with pure, dry nitrogen, and the reactants were introduced into the apparatus against a counter-current of nitrogen.

Lithium aluminium hydride (10 g.), and sodium dried ether (300 c.c.) were placed in the flask, and boron trifluoride diethyl ether complex (100 g.) was slowly added from the dropping funnel into the mixture. Diborane was immediately evolved, and care was necessary to avoid blocking the traps. When the addition was complete, the flask was warmed to drive all the diborane into the traps. Almost all of the diborane stopped in the first liquid air trap. The diborane was freed from traces of ether by attaching the trap to the vacuum line and trapping out the ether in a trap cooled by a pentane slush bath (-131°C), and allowing the diborane to pass on into a trap cooled by liquid air. The diborane prepared in this way contains a very small amount of ethyl fluoride as impurity 3·5 litres of gaseous diborane were obtained, 90% of theory.

Two other methods for the preparation of diborane were tried, and both gave yields inferior to the method chosen. The first was the reaction of sodium, borohydride with boron trifluoride diethylether complex, in diglyme, and the other was the reaction of iodine with sodium borohydride, also in diglyme. In both cases, rather large quantities of hydrogen appeared to be formed. The sodium borohydride was reasonably pure. Acid hydrolysis caused evolution of 91% of the calculated quantity of hydrogen.

Dimethylamine

Pure dimethylamine can be obtained from a commercial sample, by conversion of the latter into dimethyl-N-nitrosamine with subsequent hydrolysis back to the amine.

Dimethyl-N-nitrosamine (10 g.) were refluxed for 12 hours with concentrated hydrochloric acid (50 c.c.), and after distilling off most of the acid, the solution of the amine hydrochloride was allowed to fall onto potassium hydroxide pellets. The latter were contained in an evacuated flask, and the free amine was condensed onto more potassium hydroxide pellets in a receiving flask cooled to -78°C. The amine was then distilled onto the vacuum line through two traps cooled to -78°C and stored in a three litre bulb. The volume of dimethylamine obtained was about 2·51, corresponding to a yield of about 85%

Dimethylaminoborane

This was prepared by the method described by Burg and Randolph.[62]

Diborane (240 c.c.) was condensed onto dimethylamine (480 c.c.) contained in a flask attached to the vacuum line. The flask and contents were allowed to warm up to 20°C, and were pumped briefly to remove any slight excess of either diborane or dimethylamine. Pure nitrogen was then admitted into the vacuum line, through a needle valve, until the pressure fell to 400 mm.Hg. The reaction mixture was then heated and maintained at 130°C.

Liquid tended to reflux, but as the hydrogen was given off, the product sublimed out of the flask, and was purified by a vacuum line fractionation. Yield = 1•04 g. 85% of theory.

Methyllithium

Methyl lithium was prepared by the reaction of methyl chloride with lithium metal, in ether as solvent. The methyl chloride was supplied under pressure in a cylinder. The apparatus consisted of a one litre three-necked flask fitted with a stirrer, a cold finger condenser maintained at -78°C, and an inlet for the methyl chloride. A flow-meter was used to tell approximately the rate of passage of the methyl chloride. The cylinder was weighed before and after the experiment. The lithium was supplied as lithium shot, and was in the form of a heavy suspension in oil. The oil was washed off with hexane before use. The apparatus was purged with pure nitrogen before starting the experiment.

Lithium shot (7•0 g.) and ether 500 c.c.) were placed in the reaction flask. Methyl chloride (51 g.) was passed into the reaction mixture over a period of 5 hours. The reaction started immediately. When the addition was complete, the reaction mixture was allowed to stir for 12 hours and then the solution of methyllithium was filtered from lithium chloride and unreacted lithium metal. The methyllithium was stored and used as the ether solution. It was analysed by acid hydrolysis with subsequent measurement of the methane evolved, and was found to be 1•07 molar indicating a yield of approximately 90%.

Trimethylthallium

Trimethylthallium was prepared by the reaction of thallous iodide and methyl iodide with methyllithium.[63]

The apparatus consisted of a three-necked 500 ml. flask fitted with a stirrer, water condenser and a pressure-equilibrated dropping funnel. Methyl iodide (7·1 g.), thallous iodide (16·5 gm.), and sodium dried ether (100 ml.) were placed in the flask, and methyllithium (93·4 c.c. of 1·07 molar ethereal solution) was placed in the dropping funnel. The methyllium was added slowly, each drop producing an initial black preicpitate of finely divided thallium metal which reacted with the methyl iodide. When addition was complete, the ether was distilled in vaccuo, together with the trimethylthallium, into a two-necked flask cooled in liquid air. The trimethylthallium was conveniently stored and used as this ethereal solution, which was calibrated by acid hydrolysis, the resulting methane being measured with a Topler pump. The solution was found to be 0·69 molar, and this corresponded to a yield of about 70%.

Trimethylboron

Trimethylboron was prepared by the reaction of methylmagnesium bromide with boron trifluoride diethyl ether complex.

The apparatus consisted of a one litre three-necked flask fitted with a stirrer, a pressure-equilibrated dropping funnel and a 'cold finger' condenser. The outlet of the condenser was connected to two traps, the first of which was cooled to -78°C by an acetone/carbon dioxide slush bath, and the second was cooled in liquid air. The apparatus was purged out with pure nitrogen before the preparation was started.

The Grignard reagent MeMgBr from magnesium (9·0 g.) and methyl bromide (35 g.) in ether (250 ml.), was prepared as in the preparation of dimethylmercury. The mixture was then allowed to stir for 30 minutes after which time, boron trifluoride ether complex (30 g.) was added. Each drop caused immediate evolution of trimethylboron, most of which collected in the liquid air trap. The product was purified by passing through a trap cooled by a carbon disulphide slush bath (-110°C) to remove ether, into a trap cooled by a pentane slush bath (-135°C) to collect the trimethylboron. More volatile impurities were pumped away, and the final yield of pure trimethylboron was $\sim$ 2·5 litres, corresponding to a yield of 89%.

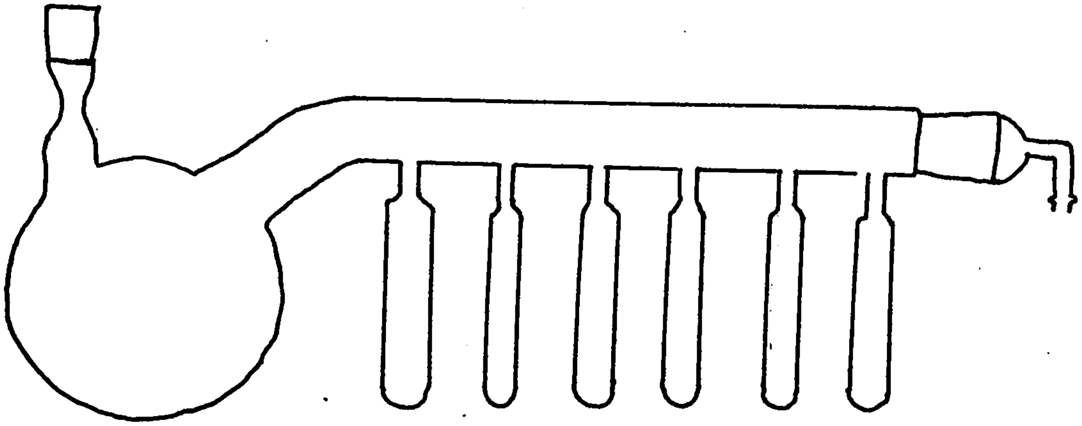
Gallium chloride

Gallium chloride was prepared by the reaction of gallium metal with chlorine gas, diluted by dry nitrogen.

The apparatus consisted of a long, thick-walled pyrex tube joined by a constricted side arm to a one-necked 500 ml. flask. The outlet of the flask was fitted with a long chimney which led to a heavy white oil bubbler.

Gallium metal, (20 g.) was placed in the tube, and the whole apparatus was purged with nitrogen. A slow stream of chlorine was then allowed to pass with the nitrogen, and the gallium metal was warmed, until it began to burn in the chlorine. The gallium chloride sublimed along the tube,

Figure I



through the constriction into the flask. When the reaction was complete, the flask was sealed off from the tube, at the constriction. The product was transferred to the apparatus shown in Fig. I , the apparatus was evacuated and sealed off at the constriction and the gallium chloride was sublimed into the ampoules. The yield was 47·5 gms., 95% of theory.

Acetoxime[64]

Hydroxylamine hydrochloride (50 g.) was dissolved in water (100 ml.) and a solution of sodium hydroxide (30 g.) in water(100 ml.) was added. The solution was cooled to 0°C and acetone (60 g.) was added slowly with shaking. On cooling, acetoxime crystallised out, and was purified by recrystallisation from cyclohexane. The yield of purified acetoxime was 25 g.

The trimethylaluminium used was a gift from Ethyl Corporation, supplied in cylinders, each containing 1/2 lb. The alkyl was purified by distillation, and was stored under nitrogen in a two-necked flask fitted with teflon sleeves.

The triethylaluminium was also a gift from Borax Consolidated Ltd., and was purified and stored as for trimethylaluminium.

Triphenylaluminium etherate had been prepared by the reaction of phenyllithium with aluminium chloride in ether, and was purified by recrystallisation from toluene.

Dimethylaluminium chloride was prepared by Mr. M. Tranah, by the distillation of methylaluminium sesquichloride to which sodium chloride had been added.

Diethylmercury was prepared (by Mr. A. Heslop) by the reaction of ethylmagnesium bromide with mercury (II) chloride and was purified by fractional distillation.

Trimethylindium was prepared by Dr. O. T. Beachley by the reaction of an indium-magnesium alloy with methyl chloride in ether.[65] The ether was removed by fractional distillation with benzene, and the trimethylindium was stored in small ampoules.

The boron trichloride was supplied in a cylinder and was used without further purification.

Diphenyl ketimine was prepared by Mr. I. Pattison by methanolysis of the product from the reaction between phenylmagnesium bromide and phenyl cyanide, and was purified by vacuum distillation.

Hydrogen cyanide had been prepared by the reaction of strong sulphuric acid with potassium cyanide, and was purified by fractional distillation.

Phenyl and alkyl cyanides were purified by fractional distillation from phosphorus pentoxide.

Hydroboration reactions of Methyl Cyanide

Reaction of methyl cyanide with diborane

This reaction was carried out several times with minor modification. A typical experiment is described below.

Diborane, generated from sodium borohydride (28 gm.) and boron trifluoridediethyl ether complex (128 gm.) in diethylene glycol dimethyl ether (300 ml.), was carried in a stream of nitrogen into methyl cyanide (44 gm.) maintained at its boiling point by a water bath. Any unreacted diborane was destroyed by passing the exit gases from the reaction through an acetone trap, and gases passing through the acetone were trapped out in liquid nitrogen (Fraction I). The volatile materials from the reaction were pumped into the vacuum line through a series of three traps cooled respectively to -46°C, -96°C and -196°C. Fraction II passed slowly through the trap at -96°C (melting toluene) and was collected in the trap cooled by liquid nitrogen (-196°C). Fraction III passed through the trap at -46°C (melting chlorobenzene) and was collected in the trap maintained at -96°C. Fraction IV was collected in the trap maintained at -46°C. Fraction V distilled at 60°C and 0•01 m.m. Hg pressure from the residue, and Fraction VI was a yellow glue, involatile up to 150°C.

Fraction I was identified by its infrared spectrum as ethylene. Some acetone, also identified by its vapour-phase infrared spectrum, was found in this trap, and after fractionation, the yield of ethylene was found to be 10 c.c. measured at N.T.P.

Fraction II was identified by its infrared spectrum and vapour-phase molecular weight as diethyl ether, which had been carried over from the boron trifluoride-diethyl ether complex by the diborane. The quantity of diethyl ether collected varied considerably from one experiment to another but was usually about 0•5 gm.

Fraction III, about 0•4 g., was found to be diethylaminodiborane $Et_2NB_2H_5$. Early samples were contaminated by diethyl ether and N-ethylborazines seen to be present from their infrared and n.m.r. spectra, and analytical figures were accordingly in poor agreement with those required for $Et_2NB_2H_5$. [Found: B, 21•2; hydrolysable H, 3•6%; M (vapour density) 99, 105. Calculated for $C_4H_{15}B_2N$ B, 21•8; hydrolysable H, 5•1%; M, 99]. In later experiments, repeated trap to trap distillation of this fraction gave ~ 50 m.g. of essentially pure diethylaminodiborane, spectroscopically indistinguishable from an authentic sample prepared from diethylamine and diborane. ν_{max} (vapour phase, 2 cm. Hg. pressure, KBr cell). 3373m, 2985vs, 2950s, 2899s, 2541vs, 2478vs, 2404m, 2370m, 1923m, 1880s, 1634vs, 1555m, 1473sh, 1457sh, 1449vs, 1387w, 1344s, 1305s, 1201sh, 1193vs, 1142sh, 1133s, 1072sh, 1067vs, 958sh, 953vs, 891s, 792s, 715s, cm^{-1}.

The mass spectrum of the diethylaminodiborane was recorded and accurate masses measured for the major peaks in the spectrum. The impurities present gave rise to spurious peaks, and the accurate masses of these peaks showed them to originate from N ethylborazines. The mass spectroscopic data for the major peaks of diethylaminodiborane are given in Table V. Peaks due to the ^{10}B isotope are ignored.

TABLE V

Fragment	Experimental Mass	Calculated Mass	Error (p.p.m.)	Intensity
$C_4H_{14}B_2N$	98·13177	98·13123	5·5	6·4
$C_4H_{12}BN$	85·10566	85·10628	7·3	31·5
$C_4H_{11}BN$	84·09923	84·09846	9·1	66·4
C_3H_9BN	70·08292	70·08281	1·6	100
$C_2H_8B_2N$	68·08564	68·08429	19·9	very weak
C_3H_7BN	68·06784	68·06716	10·0	43·7
C_2H_5BN	54·05114	54·05151	7·6	30·0
CH_3BN	40·03589	40·03585	1·0	30·9

The proton magnetic resonance spectrum was recorded in benzene solution, with tetramethylsilane as internal reference. The results obtained are shown in Table VI.

TABLE VI

	Multiplicity	Assignment	τ^{x}	J (c.p.s.)
Peak 1	Triplet	$C\text{-}CH_3$	$8{\cdot}9_0$	7·2
Peak 2	Quartet	$N\text{-}CH_2\text{-}C$	$7{\cdot}2_2$	7·2
Peak 3	Quartet	B-H	$8{\cdot}5_6$	127

^{x} τ T.M.S. = 10·00

The ^{11}B muclear magnetic resonance spectrum was recorded in toluene solution, with trimethylborate as internal reference compound. A triplet of doublets was obtained 36•8 p.p.m. to high field of the reference with J(triplet) = 130 c.p.s. and J(doublet) = 31 c.p.s.

Preparation of diethylaminodiborane and ethylaminodiborane.[66]

Diborane (224 N c.c., 10 m.mole) was condensed onto diethylamine (0•73 gm., 10 m.mole) in a glass vessel which was sealed off from the vacuum line. The mixture was heated at 90°C in an oven for 24 hours and was then opened onto the vacuum line. The reaction mixture was passed through a trap at -64°C into a trap at -96°C, and anything volatile at -96°C was pumped away. The bulk of the product collected in the trap at -96°C and the infrared, nuclear magnetic resonance and mass spectra were identical with that of the unknown compound.

Ethylaminodiborane was prepared by an identical method, and the spectra of this compound were all significantly different from those of diethylaminidiborane. The infrared spectrum, vapour phase, showed bands at 3401s, 2976s, 2903m, 2538vs, 2475vs, 2341w, 1905m, 1635vs, 1572w, 1422v,br, 1278w(P,Q,R.), 1183vs, 1170vs, 1161vs, 1152vs, 1134sh, 1100vs, 1093vs, 1087sh, 1058sh, 1053vs, 1043sh, 946vs, 795m,br, 717m,br. cm^{-1}.

The proton magnetic resonance spectrum was recorded in benzene solution, with tetramethylsilane as internal reference. The results obtained are shown in Table VII. The peak due to N-H was not seen.

TABLE VII

	Multiplicity	Assignment	τ *	J.c.p.s.
Peak 1	Triplet	C-CH_3	8•79	7•2
Peak 2	Poorly defined Quarter	N-CH_2-C	7•32	-
Peak 3	Quartet	BH	8•81	128

* τ T.M.S. = 10•00

The ^{11}B nuclear magnetic resonance spectrum was recorded in toluene solution, with trimethyl borate as internal reference compound. A triplet of doublets was obtained 41•5 p.p.m. to high field of the reference with J(triplet) = 129 c.p.s., and J(doublet) = 29 c.p.s.

Fractions IV, V and VI

Fraction IV was found to be N triethylborazine. Found: C, 45•71; H, 11•54 and B, 19•83%. Calculated for $C_6H_{18}B_3N_3$, C, 43•8; H, 11•2; and B, 19•70%.

Crude samples of this fraction apparently contained N-diethylborazine, as revealed by a weak N-H stretching band in their infrared spectra at ~ 3400 cm^{-1}, and also by the presence of small quantities of ammonia on alkaline hydrolysis.

Fraction V, a colourless viscous liquid, was not fully characterised. The analytical figures obtained were as follows: C, 45•78; H, 10,34; B, 17•40; N, 26•43%. M(cryoscopic in benzene) 314, 260, 280. These figures except for the molecular weight, are in good agreement with $(Et_3N_3B_3H_2)_2NEt$ which requires C, 45•24; H, 10•58; B, 17•47; and N, 26•39%; M, 372. The infrared spectrum (liquid film) shows the following peaks. 2967vs, 2915s, 2882s, 2469s,br, a region of very strong almost continuous absorption from 1500-1400, 1372vs, 1350vs, 1333vs, 1302vs, 1253vs, 1238s, 1208m, 1190s, 1135s, 1117s, 1101s, 1079s, 1022m, 988w, 888vs, 805m, 714m, 695m cm^{-1}. Alkaline hydrolysis gave ethylamine, ammonia and hydrogen.

A preliminary mass spectroscopic investigation does not support the formulation of this fraction as $(Et_3N_3B_3H_2)_2NEt$ as discussed later.

Fraction VI was a yellow glue, whose infrared spectrum was very similar to that of Fraction V, but the bands were much less well defined. No analytical figures were obtained, but qualitative alkaline hydrolysis yielded ethylamine, ammonia and hydrogen.

<u>Reaction of methyl cyanide with N-triethylborazine</u>.

N-triethylborazine (1•7755 gm. 10•76 m.mole) and methyl cyanide (0•4719 gm. 11•50 m.mole) were heated in a sealed tube at 150° for 3 hours. Methyl cyanide (0•4696 gm., 99•5% recovery) and N-triethylborazine (1•4385 gm, 81•0% recovery) were recovered with an unidentified gas (32•75 c.c. 1•46 m. mole) on opening the tube. The involatile residue had an infrared spectrum identical to that of the product from the thermal decomposition of N-triethylborazine. A repeat experiment, at 40°C in the presence of diethyl ether also gave quantitative recovery of methyl cyanide.

Reaction of ethylamine with N-triethylborazine.

In a preliminary experiment, ethylamine (88·3 N c.c., 3·94 m. mole) was condensed onto N-triethylborazine (1·3 gm., 7·9 m.mole) in a tube which was sealed off from the vacuum line. After heating at 75°C for three hours, hydrogen (63·8 c.c., 2·85 m.mole), ethylamine (0·373gm., 3·05 m.mole) and N-triethylborazine (0·9 gm., 5·45 m.mole) were recovered, on opening the tube.

Ethylamine (88·3 N c.c., 3·94 m.mole) was condensed onto N-triethylborazine (1·2843 gm., 7·78 m.mole) in a tube which was sealed off from the vacuum line. After heating at 180°C for twelve hours, hydrogen (89·6 N c.c. 4·0 m.mole), ethylamine (43·9 N c.c. 1·96 m.mole) and N-triethylborazine (1·041 gm., 6·31 m.mole) were recovered on opening the tube. The infrared spectrum of the involatile residue had features in common with the infrared spectrum of Fraction V from the reaction of methyl cyanide with diborane. An additional very strong, sharp absorption was present in the 3400 cm^{-1} region, which was in the region characteristic at N-H stretching vibrations.

Reaction of methyl cyanide with trimethylamineborane $Me_3N_2BH_3$.

Diborane (174·5 N c.c., 7·785 m.mole), and trimethylamine (349 N c.c, 15·6 m.mole) were condensed onto methyl cyanide (0·319 gm., 7·8 m.mole) in a tube which was sealed off from the vacuum line. No reaction had occurred after two weeks at room temperature, and the methyl cyanide was recovered almost quantitatively after heating at 70°C for one hour.

Reaction of methyl cyanide with dimethylaminoborane $(Me_2NBH_2)_2$.

Dimethylaminoborane (0•3641 gm., 3•20 m.mole) and methyl cyanide (0•2877 gm., 7•0 m.mole) were heated together at 60°C for twelve hours in a sealed tube. There was no reaction, and the starting compounds were recovered unchanged, in 98% yield. The reaction was repeated, using ether as solvent, with the same result.

Reaction of methyl cyanide with dichloroborane $HBCl_2$.

The dichloroborane (55•4 mole) was prepared "in situ" by allowing diborane (205•7 N.c.c., 9•18 m.mole) to equilibrate with boron trichloride (829 c.c., 37•0 m.mole) in the presence of diethyl ether. Methyl cyanide (2•257 gm., 55•05 m.mole) was then condensed into the reaction vessel, and the mixture allowed to warm slowly to room temperature. After twelve hours at room temperature, the volatile materials were pumped away leaving an involatile residue. Methyl cyanide - boron trichloride adduct MeCN, BCl_3, identified by its I.R. spectrum and melting point, was sublimed from the residue and a colourless liquid could be distilled in vacuo, leaving a yellow involatile glue. The infrared spectrum of the liquid showed broad intense absorption at 7 μ, characteristic of borazine ring vibrations. The following analytical figures were obtained: B, 13•49; Cl, 29•66; hydrolysable H, 0•22%.
Calculated for $Et_3N_3B_3Cl_3$. B, 12•1, Cl, 39•8; hydrolysable H, 0%.
Calculated for $Et_3N_3B_3HCl_2$. B, 14•2; Cl, 30•0; hydrolysable H, 0•43%.
Hydrolysis of the yellow glue yielded hydrogen chloride gas, hydrogen, ethylamine and ammonia.

Reaction of methyl cyanide with monochlorborane, H_2BCl.

The monochloroborane (51•7 m.mole) also was prepared "in situ" by allowing diborane (385•3 N c.c, 17•2 m.mole) to equilibrate with boron trichloride (387•5 N c.c, 17•3 m.mole) in the presence of diethyl ether (10 c.c.) over a period of two hours. Methyl cyanide (2•103 gm., 51•3 m.mole) was condensed into the reaction vessel, and the mixture allowed to warm slowly to room temperature. After eighteen hours at room temperature, the volatile materials were pumpedaway, leaving a viscous residue. When this residue was heated at 90^o, under vacuum, a very small quantity of methyl cyanide-boron trichloride adduct was obtained. The infrared spectrum of the residue showed absorptions at ~ 2400, ~2300, ~1650 and ~ 1450 cm^{-1}, which can be assigned to B-H, C ≡N, C=N stretching and borazine ring vibrations respectively. Alkaline hydrolysis yielded hydrogen, and an approximately equimolar mixture of ammonia and ethylamine.

Reactions of organoaluminium compounds with cyanides

Reaction of t-butyl cyanide with trimethylaluminium

The adduct $Bu^tCN, AlMe_3$, m.p. 61°, was conveniently prepared by treating t-butyl cyanide with an excess of trimethylaluminium at -78°, allowing the mixture to warm to room temperature, and removing residual trimethylaluminium by pumping. It was purified by vacuum sublimation at 55-60°. [Found: 17·1; hydrolysable methyl, 29·2%; M, 165. $C_8H_{18}AlN$ requires Al, 17·4; hydrolysable methyl, 29·0%; M, 155]; ν_{max} (benzene solution, 450-200 cm^{-1}.) 412m, 262s, 240s cm^{-1}.

Thermal decomposition of $Bu^tCN, AlMe_3$. When a sample of the adduct was heated at 150° for 3 hrs. it rearranged virtually completely to the alkylideneamino derivative, $(Bu^tCMe{:}N{\cdot}AlMe_2)_2$ m.p. 113°, purified by vacuum sublimation at 110-120°, only a trace of involatile residue remaining. [Found: Al, 17·5; C, 61·3; H, 11·6%; M, 340. $C_{16}H_{36}Al_2N_2$ requires Al, 17·4; C, 61·9; H, 11·7%; M, 310]; ν_{max} (nujol mull) 1629vs, 1269w, 1192s, 1136s, 1035w, 971w, 943w, 909w, 844w, 776m, 734vs, 684vs, 582w, 546m, 512m, 448s, 394s, 364s, 312s cm^{-1}. The compound suffered only slight surface decomposition on exposure to air, and was hydrolysed only very slowly by dilute sulphuric acid, so that the hydrolysis method was not convenient for its analysis. It was effectively unchanged after being heated at 280° for 2 hrs. under nitrogen, and did not react further with trimethylaluminium at this temperature.

Reaction of t-butyl cyanide with triethylaluminium

Equimolar quantities of t-butyl cyanide and triethylaluminium reacted exothermically at room temperature to form the liquid adduct $Bu^tCN, AlEt_3$, which could be distilled unchanged at 70° under vacuum. [Found: Al, 13•8; hydrolysable ethyl, 43•6%. $C_{11}H_{24}AlN$ requires Al, 13•7; hydrolysable ethyl, 44•2]; ν_{max} (benzene solution 450-200 cm^{-1}.); 438s, 412s, 366w, 336m(br), 272m(br), 228w cm^{-1}.

Thermal decomposition of $Bu^tCN, AlEt_3$. Samples of adduct were unchanged when heated at 125-135° for several hours, but at 155-160° during 5 hrs. there was smooth evolution of ethylene (1 mol per mol adduct), the product being a liquid which could be distilled at 82° under vacuum and which was identified as neopentylideneaminodiethylaluminium dimer, $(Bu^tCH:N \cdot AlEt_2)_2$. [Found: Al, 14•2; hydrolysable ethyl, 35•3%; M, 323; $C_{18}H_{40}Al_2N_2$ requires Al, 14•1; hydrolysable ethyl, 34•3%; M, 338]; ν_{max} (liquid film) 3330vw, 2959s, 2933s, 2899s, 2857s, 2793w, 2717w, 1760vw, 1670msh, 1656vs, 1626m, 1555vw, 1477s, 1464s, 1410s, 1385w, 1363s, 1270vw, 1229m, 1209m, 1202m, 1190m, 1143vw, 1107w, 1070m, 1033m, 986vs, 950s, 919s, 893s, 778vs, 681vs, 649vs, 630sh(br), 606sh(br), 559m, 454ms cm^{-1}. Benzene Solution 454vs, 398vs, 385vs, 319m,br. cm^{-1}.

Reaction of t-butyl cyanide with triphenylaluminium-diethyl ether complex.

Triphenylaluminium-ether complex (2•7 g., 8•1 m. mole) in benzene (20 c.c.) was treated with t-butyl cyanide (0•6 g., 8•2 m mole) and warmed to 50°. Solvent was removed under reduced pressure until crystals of the adduct, $Bu^tCN,AlPh_3$, m.p. 114°, separated [Found: Al, 7•9%. $C_{23}H_{24}AlN$ requires Al, 7•9%]; ν_{max} (benzene solution, 450-200 cm^{-1}) 459vs, 424s, 417sh, 333s, 251mbr cm^{-1}. This compound could not be vacuum sublimed without simultaneous rearrangement taking place.

Thermal decomposition of $Bu^tCN, AlPh_3$. Samples of the adduct rearranged completely during 3 hrs. at 170° to the benzylideneamino derivative $(Bu^tCPh:N\cdot AlPh_2)_2$, a crystalline solid which slowly decomposed without subliming or melting at 220° and which was purified by crystallisation from benzene [Found: Al, 7•9, hydrolysable phenyl, 43•8%; M, 684. $C_{46}H_{48}Al_2N_2$ requires Al, 7•9; hydrolysable phenyl, 45•1%; M, 682]; ν_{max} (nujol mull) 1616vs, 1422s, 1279w, 1264w, 1247w, 1205m, 1155w, 1088s, 1074s, 1040w, 1029w, 1004w, 998w, 974s, 970sh, 913w, 824w, 781s, 750w, 734vs, 718sh, 705vs, 682vs, 675vs, 650s, 622w, 608s, 529s, 482vs cm^{-1}; (benzene solution) 455sh, 407w, 352s, 330s cm^{-1}.

Reaction of t-butyl cyanide with dimethylaluminium chloride

The adduct, $Bu^tCN,AlMe_2Cl$, m.p. 84°, from equimolar quantities of the components, was purified by vacuum sublimation at 85° [Found: Al, 14•9; hydrolysable methyl, 16•3%. $C_7H_{15}AlClN$ requires Al, 14•9; hydrolysable methyl, 17•2%]; ν_{max} (benzene solution, 450-200 cm^{-1}). 439vs, 407s, 290sh and 274m,br cm^{-1}.

Thermal decomposition of $Bu^tCN, AlMe_2Cl$. Little decomposition of the adduct was detected at temperatures below 220°, but complete rearrangement occurred during 6 hours at 240°, and a colourless, very air-sensitive solid could be vacuum sublimed from the reaction mixture at 145°. This was identified as $(Bu^tCMe{:}N{\cdot}AlMeCl)_2$, m.p. 130°. [Found: Al, 14•9; hydrolysable methyl, 8•4%; M, 365. $C_{14}H_{30}Al_2Cl_2N_2$ requires Al, 14•9; hydrolysable methyl, 8•6%; M, 351]; ν_{max} (CCl_4 solution) 1967s, 1874sh, 1625vs, 1473m, 1422w, 1372s, 1273w, 1261m, 1203s, 1147s, 1068m, 1045m, 981w, 942w, 871s, 861sh, 691s, 671s, 568w, 534m, 494sh, 467m cm^{-1}; (benzene solution) 439s, 405s, 382sh, 315 m,br cm^{-1}. After the sublimation about half the reaction mixture remained as an involatile yellow glue.

Reaction of t-butyl cyanide with dimethylaluminium hydride.

A solution of dimethylaluminium hydride (10 m mole) in hexane (15 c.c.) was added by syringe to t-butyl cyanide (0•83 g. 10 m mole) at room temperature. A vigorous exothermic reaction occurred. Removal of the solvent afforded crystals of neopentylideneaminodimethylaluminium dimer, $(Bu^tCH{:}N{\cdot}AlMe_2)_2$, m.p. 89°, purified by vacuum distillation/sublimation at 110°. [Found: Al, 19•0; hydrolysable methyl, 20•9%; M, 275. $C_{14}H_{32}Al_2N_2$ requires Al, 19•1; hydrolysable methyl, 21•3%; M, 282]; ν_{max} (nujol mull) 1661vs, 1412s, 1274w, 1192vs, 1035s, 946m, 924m, 898s, 779vs, 689vs, br, 580s, 508m; (benzene solution) 449s, 380vs, 345w, 306sh, 297s cm^{-1}.

Reaction between Hydrogen Cyanide and Dimethylaluminium Hydride. When dimethylaluminium hydride (0•311 g., 5•4 m mole) in hexane (8 c.c.) was treated with hydrogen cyanide (120 N c.c., 5•4 m mole) at -78°, hydrogen (121 N c.c., 5•4 m mole) was evolved and dimethylaluminium cyanide $(Me_2AlCN)_4$, m.p. 89° was isolated from the mixture and identified by its infrared spectrum.[67]

Reaction of methyl cyanide with dimethylaluminium hydride

Dimethylaluminium hydride (1•137 g., 19•6 m.mole) in hexane, (30 ml.) was added by syringe to methyl cyanide (0•402 g., 9•8 m mole) in 30 ml. hexane at room temperature. The heat of reaction caused the solvent to boil, and the mixture was subsequently kept at this temperature for 15 minutes. The hexane was then removed under vacuum, leaving an involatile viscous oil which had bands at ~1770 and 1640 cm^{-1}. in the infrared spectrum which indicated that reaction was incomplete. After being heated at 145^{o} for a further 30 min., the residual glue was hydrolysed with strong sodium hydroxide solution to give methane and ethylamine together with some hydrogen and ammonia.

Reactions of Organo-gallium compounds with cyanides

Preparation and thermal decomposition of MeCN, $GaMe_3$.

The adduct MeCN, $GaMe_3$, previously described by Coates and Hayter,[1] was prepared by condensing trimethylgallium (430 N c.c., 19·2 m mole) onto methyl cyanide (0·787 gm., 19·2 m mole) ν_{max}(liquid film). 2941s, 2899m, 2857sh, 2308m, 2282m, 1429s,br, 1377s, 1189vs, 1038s,br, 1027sh, 1010sh, 934s, 734vs,br, 660w,br, 556vs, 519w cm^{-1}.

A sample of the adduct was sealed off in a tube. Heating at 120° caused slight discolouration and at 145°C methane (420 N.c.c., 98% reaction) was evolved, leaving a yellow solid insoluble in all solvents except acetone. Acid hydrolysis did not result in the formation of acetone, $\nu_{max.}$ (nujol mull), 2164vs, 1577s, 1189m, 1143m, 1002w, 930 w, 714vs,br, 637w, 571s,br, 532s,br. cm^{-1}.

Reaction of phenyl cyanide with trimethylgallium

The adduct PhCN, $GaMe_3$ m.p. 25-27°C, was prepared by condensing trimethyl-gallium (364·0c.c., 16·24m mole) onto phenyl cyanide (1·675g, 16·24 m mole). The adduct is dissociated in the vapour phase, so purification was not attempted. (Found: Ga, 31·9%. PhCN, $GaMe_3$ requires Ga, 32·1%). ν_{max} (liquid film). 3058m, 2941vs, 2899vs, 2857sh, 2260vs, 1961w, 1894w, 1811w, 1764w, 1681w, 1597s, 1490s, 1449vs, 1387w, 1336w, 1290m, 1189vs, 1184m, 1096w, 1068m, 1036m, 1027s, 1009s, 1002sh, 926m, 842w, 757vs, 735vs,br, 686vs, 587vs, 562vs, 531vs, 463m,br. cm^{-1}. Vapour pressure, 2·9 mm. at 20°C.

Thermal decomposition of PhCN, $GaMe_3$.

A sample of the adduct was heated at 118°C for 15 hours. The reaction mixture became red-brown, and on cooling needle-shaped crystals appeared. A little trimethylgallium was recovered but most of it remained in the reaction vessel. The crystals were recrystallised from toluene. (Found: C, 81·0, H, 4·89%. $C_{21}H_{13}N_3$ requires C, 81·5, H, 4·85%). m.p. 23°C.

Reaction of t-butyl cyanide with trimethylgallium

The adduct Bu^tCN, $GaMe_3$, was prepared by reaction of equimolar quantities of t-butyl cyanide with trimethylgallium. It is largely dissociated in the vapour phase, and can be rapidly pumped into a vacuum system at room temperature presumably as the free components. Purification was not attempted. (Found: Ga, 35·0%. $C_8H_{18}Ga$ requires Ga 35·4%). m.p. $< 20^oC$. ν_{max} (liquid film) 2976vs, 2941vs, 2907sh, 2878sh, 2266s, 1486s, 1466s, 1357s, 1247s, 1212s, 1193s, 1070br, 1035sh, 1012s, 940w, 738vs,br, 691vs, 582vs,br, 557vs,br, 535vs,br. cm^{-1}.

Attempted thermal decomposition of Bu^tCN, $GaMe_3$.

Several experiments, each under differing conditions were carried out.

(a) A sample of the adduct was heated in a sealed tube at temperatures ranging from 120° - 200°. On cooling the adduct was almost quantitatively pumped unchanged into the vacuum line, leaving a very small brown residue.

(b) Trimethylgallium (328 c.c., 14•63 m mole) and t-butyl cyanide (0•61 g., 7•315 m mole) were heated at 150°C for 12 hours in a sealed tube. On opening the tube, the adduct and excess trimethylgallium were recovered unchanged.

(c) Trimethylgallium-t-butyl cyanide in benzene solution was heated at 150° for 12 hours in a sealed tube. On opening the tube, the reactants were recovered unchanged.

Reaction of trichloroacetonitrile with trimethylgallium

Trimethylgallium (224 c.c., 10 m mole) was condensed onto trichloroacetonitrile (1•44 gm., 10 m mole) in a tube which was sealed off from the vacuum line. On warming to room temperature, 25°C, the reaction mixture turned brown, and the reaction product after heating at 100°C for 12 hours was a deep brown viscous liquid. Hydrolysis of this liquid gave a solution which precipitated silver chloride from a silver nitrate/nitric acid mixture.

Reaction of t-butyl cyanide with triethylgallium

The adduct $Bu^tCN, GaEt_3$, from equimolar quantities of t-butyl cyanide and triethylgallium was a colourless liquid only slightly volatile at room temperature. (Found: Ga, 28•8%. $C_{11}H_{24}GaN$ requires Ga 29•17%). ν_{max} (liquid film) 2273 cm^{-1}. m.p. $<$ 20°C.

Thermal decomposition of $Bu^tCNGaEt_3$.

A sample of the adduct (3•06 gm., 12•73 m mole) was heated at 150°C for 15 hours in a sealed tube. On opening the tube, ethylene (57 c.c., 2·54 m mole) was recovered. On heating the tube and contents at 180°C for a further 15 hours, another 200 c.c. ethylene, corresponding to ~ 90% reaction, was recovered. The product, a liquid which could be distilled from a boiling water bath under vacuum, was identified as diethylneopentylideneaminogallium dimer $(Bu^tCH{:}NGaEt_2)_2$. (Found: Ga, 32·8%, M (cryoscopic in benzene) 400. $C_{18}H_{40}Ga_2N_2$ requires Ga, 33·0%, M, 424); ν_{max} (liquid film). 3311w, 2950vs, 2902vs, 2865vs, 2725m, 1658vs, 1479s, 1466s, 1424m, 1368s, 1236w, 1205m, 1061w, 1034m, 1000s, 961m, 942sh, 935m, 923w, 894s, 778s, 709br, 671sh, 658vs, br, 563s, 549s, 513s, 485s, 409m,br. cm^{-1}. (Benzene solution) 461vs, 429sh, 369vs, 341m, 278w,br, 246w,br. cm^{-1}.

Reaction of phenyl cyanide with triethylgallium

Phenyl cyanide (1·12g, 10·83 m mole) and triethylgallium were mixed at -78°C and allowed to warm to room temperature. The heat of reaction did not cause a significant increase in temperature. The product, a colourless liquid going yellow on standing, was identified as the adduct, $PhCN,GaEt_3$ (Found: Ga 26·7%. $C_{13}H_{20}NGa$ requires Ga 26·9%), ν_{max} (liquid film). 2915vs, 2882vs, 2849vs, 2793w, 2258vs, 1595w, 1488w, 1462sh, 1447m, 1414w, 1368w, 1332w, 1287w, 1259w, 1232w, 1180sh, 1177w, 1161w, 1093m, 1067w, 1025m, 998m, 993sh, 953m, 924m, 797w,br, 756vs, 697w, 683vs, 649s,br, 550vs, 533vs,br 471w,br. cm^{-1}.

Thermal decomposition of $PhCN,GaEt_3$.

When a sample of the adduct, $PhCN,GaEt_3$, (2•5 gm., 9•61 m mole) was heated at 150°C for 15 hours, ethylene (183 c.c., 85% of theory) was evolved, and the product was a viscous liquid, which crystallised on standing. Benzylideneaminodiethylgallium dimer, $(PhCH{:}NGaEt_2)_2$, was obtained as a pale yellow solid by sublimation from the reaction mixture. (Found: Ga, 30•2; C, 55•5; H, 6•5%; M (cryoscopic in benzene), 434. $C_{22}H_{32}Ga_2N_2$ requires Ga, 302; C, 56•9; H, 6•69%; M, 464). m.pt. 118°C. ν_{max} (nujol mull) 3081m, 3058m, 3021m, 1688m, 1633vs, 1600s, 1585s, 1520w, 1493w, 1416w, 1309m, 1289w, 1259w, 1233w, 1202s, 1176w, 1155w, 1101w, 1076m, 1026m, 1005s, 965sh, 960s, 934m, 841vs, 744vs, 699vs, 685vs, 654vs, 617w, 551vs,br, 514s,sh, 509s, 482s, 467s, 417m,br. M.Pt.68° Hydrolysis with weak acid gave benzaldehyde, identified as its 2-4-dinitrophenylhydrazone.

Reaction of methyl cyanide with triethylgallium

The adduct, $MeCN,GaEt_3$ prepared by reaction of equimolar quantities of methyl cyanide with triethylgallium was a colourless liquid, only slightly volatile at room temperature. $\nu_{max.}$ (liquid film). 2933vs, 2899vs, 2857vs, 2808w, 2307m, 2279m, 1464sh, 1456m, 1420m, 1393w, 1374m, 1263w, 1235w, 1166w, 1100m, 1053s, 999s, 956m, 931m, 898m, 807m, br, 657vs,br, 635sh, 534vs, br. cm^{-1}.

Reaction of benzophenone with trimethylgallium

Trimethylgallium (258•4 c.c., 11•53 m mole) was condensed onto benzophenone (2•10 gm, 11•53 m mole) in a tube which was sealed off from the vacuum line. On warming to room temperature, the benzophenone dissolved in the trimethylgallium to give a green viscous solution, and after heating at 125° for 15 hours, the reaction product was a glass which crystallised on cooling. A little methane was recovered on opening the tube, and the solid product, purified by recrystallisation from hexane, was identified as dimethylgallium diphenylmethyl methoxide $(Me_2GaOCMePh_2)_2$. (Found: Ga, 23•5%. $C_{32}H_{38}Ga_2O_2$ requires Ga 23•6%. ν_{max} (nujol mull). 3096w, 3058m, 3021s, 1667w, 1660w, 1582w, 1490w, 1314m, 1297w, 1277w, 1231s, 1206vs, 1199vs, 1189m, 1178m, 1111m, 1096s, 1087sh, 1075w, 1063vs, 1049vs, 1025s, 1001w, 982w, 965w, 938sh, 924vs, 910vs, 848w, 834m, 770vs, 760vs, 751vs, 706vs, 696vs, 634vs, 621sh, 601sh, 594sh, 586vs, 536s, 466vs, 425m,br. M.Pt.

The product could be sublimed at 0•01 m.m. Hg. pressure from an oil bath at 140°C.

Reaction of ethyl isocyanate with trimethylgallium

Trimethylgallium (422 c.c, 18•84 m mole) was condensed onto a solution of ethyl isocyanate (1•34 gm., 18•84 m mole) in hexane (30 ml.) in a double Schlenk tube. On warming to room temperature, reaction proceeded slightly exothermically. The mixture was heated to reflux temperature to ensure complete reaction. The product was obtained as a viscous involatile oil on removal of the hexane, and complete purification was impossible. No reaction with 4-dimethylaminopyridene was observed. Hydrolysis of the product yielded N-ethylacetamide.

Reaction of diphenylketimine with trimethylgallium.

Trimethylgallium (190•5 c.c., 8•50 m mole) was condensed onto diphenylketimine (1•54 gm., 8•51 m mole) in a tube, which was sealed from the vacuum line. The tube was heated at 94°C for 15 hours, and on opening, methane (170 c.c.) was recovered. The product was obtained as large crystals from hexane. (Found: C 63•9, H 5•97, Ga 25•3%, $C_{30}H_{32}Ga_2N_2$ requires C 64•2, H 5•71, Ga 25•0%). ν_{max} (Nujol mull). 1626m, 1605sh, 1577m, 1318w, 1282w, 1266w, 1203sh, 1193m, 1160w, 1078w, 1030w, 1003vw, 989vw, 910vw, 951m, 923w, 911m, 784s, 742s, 734sh, 724s, 699vs, 667s, 577sh, 570s, 529s, 451s cm^{-1}.

Reaction of diphenylketamine with triethylgallium

Triethylgallium (1•4gm., 8•92 m mole) was condensed onto diphenylketimine (1•61 gm., 8•92 m mole) in a tube which was sealed off from the vacuum line. The tube was heated at 100° for 36 hours, and on cooling to room temperature, brown-yellow crystals were deposited from the melt. The tube was opened, and ethane (192 N c.c., 8•57 m mole, 96% reaction) was recovered. The product was obtained as small white crystals from hexane at -80°C. (Found: C, 65•5; H, 6•26; Ga, 19•8%; M (cryoscopic in benzene), 649. $C_{34}H_{40}Ga_2N_2$ requires C, 66•2; H, 6•49; Ga, 22•01%; M, 616). ν_{max} (Nujol mull) 1613vs, 1577sh, 1427m, 1316m, 1287m, 1267m, 1235w, 1185w, 1160w, 1076m, 1029m, 1003m, 997sh, 951s, 935m, 925m, 912m, 846w, 780vs, 704sh, 700vs, 671vs, 660vs, 543s, 529s, 514s, 505s, 454s, cm^{-1}.

Reactions of organometallic compounds with acetoxime

Reaction of trimethylboron with acetoxime

Trimethylboron (303·4 c.c., 13·5 m mole) was condensed on to acetoxime (0·99 gm., 13·5 m mole) in a tube. At room temperature, the pressure in the tube showed all the trimethylboron to be in the gas phase, and no visible reaction occurred. The tube was sealed and heated at 95-100°C for twelve hours. Methane (290·3 c.c, 13·0 m mole) and dimethyl(isopropylideneaminoxy)boron, $Me_2C{:}NOBMe_2$, a volatile colourless crystalline solid, m.pt. °C were produced. (Found: C, 52·0; H, 10·4; N, 12·5%; M (vapour density at 85°), 112·4; M (cryoscopic in benzene), 147. $C_5H_{12}BNO$ requires C, 53·1; H, 10·6; N, 12·4; M, 112·8). Vapour pressure (23-71°C) given by $\log_{10}P_{mm} = 14{\cdot}340 - \frac{4267}{T}$, corresponding to a value of 2·1 m.m. at 20°C and an extrapolated b pt. of 99°C. ν_{max} (vapour phase, 70°C) 1663w, 1433w, 1385s, 1333sh, 1323vs, 1294s, 1252s, 1188w, 1160s, 1152s, 1066m, 966sh, 941m, 882w, 820w, 733vw,br; (nujol mull) 1649m, 1297vs, 1239vw, 1193w, 1163s, 1104sh, 1080sh, 1070vs, 1046sh, 1030vs, 1000vs, 985sh, 939sh, 974m, 812s, 733s, 645w, 622w, 580m, 567w, 539s, and 457m, cm^{-1}. This last band was the only one detected in the range 500-200 cm^{-1}. The compound was readily soluble in such solvents as benzene, cyclohexane, and carbon tetrachloride but was immediately hydrolysed by water. When exposed to air, the crystals suffered slow surface hydrolysis.

Reaction of diborane with acetoxime

Diborane (132·1 c.c., 5·9 m mole) was condensed at -196°C on to acetoxime (0·86 gm., 11·8 m mole) in a tube which was then sealed from the vacuum line. The tube was allowed to warm to room temperature, when the reaction mixture was a viscous liquid which slowly evolved bubbles of gas. The heat of the reaction raised the temperature of the mixture noticeably above room temperature, and at about 30° or 40°C there was a sudden flash and a black powdery involatile residue covered the walls of the tube. Hydrogen, methane, ethylene and hydrogen cyanide were detected among the involatile reaction products.

Reaction of trimethylaluminium with acetoxime

Acetoxime (1·6 gm., 22 m mole) in hexane (25 c.c.) was slowly added by syringe to trimethylaluminium (1·6 gm., 22 m mole) in hexane (25 c.c.) cooled to -78°C in one limb of a double Schlenk tube, the apparatus being well shaken to promote mixing. A vigorous reaction proceeded spontaneously with evolution of methane. After concentration of the solution by removal of some solvent by vacuum distillation, very small crystals of dimeric methyl(isopropylideneaminoxy)aluminium, $(Me_2C{:}NOAlMe_2)_2$ separated at -78°C. The product, purified by vacuum sublimation at 55°C had m.pt. 71·5°C. (Found: Al, 20·9; hydrolysable methyl, 23·0%; M(cryoscopic in benzene), 268. $C_{10}H_{24}Al_2N_2O_2$ requires Al, 20·9; hydrolysable methyl, 23·0%; M, 258). ν_{max} (nujol mull) 1635m, nujol, 1282s, 1190vs, 1092vs, 1078sh, 1028vs, 889w, 853m, 766sh, 735vs,br, 561w, 538w, and 491m. cm^{-1}.

The product was readily soluble in benzene, hexane and carbon tetrachloride and reacted with solvents containing hydroxyl groups. Extremely sensitive to air and moisture, it inflamed in contact with water or when placed on tissue paper.

Reaction of dimethyl(isopropylideneaminoxy)aluminium with 4-dimethylamino pyridine.

Dimethylaminopyridine (0•4 gm., m mole) dissolved in toluene (25 c.c.) was added by syringe to a solution of dimethyl(isopropylideneaminoxy) aluminium (0•4 gm. m mole). in hexane (20 c.c.). All solvent was pumped away, and the residue recrystallised from a mixture of benzene (5 c.c.) and hexane (30 c.c.). The solid was found to be a mixture consisting largely of dimethylaminopyridine and some of the aluminium compound, since the hydrolysable methyl content was 16•0% low for the adduct, and the infrared spectrum showed absorptions due only to the free components.

Reaction of trimethylgallium with acetoxime

Trimethylgallium (260 c.c., 11•6 m mole) was condensed at -196° on to a frozen solution of acetoxime (0•85 gm., 11•6 m mole) in hexane (25 c.c.). Reaction proceeded vigorously when the mixture was warmed to -78°C and methane (260 c.c., 11•6 m mole) was evolved. The product, $(Me_2C:NOGaMe_2)_2$ crystallised as very small needles at -78°C, and was purified by vacuum sublimation at 60°C; m.pt 90-91°. [Found: Ga, 40•4; C, 34•1; H, 7•0%; M (cryoscopic inbenzene), 339. $C_{10}H_{24}Ga_2N_2O_2$ requires Ga, 40•6; C, 349; H, 7•0%; M,342]. ν_{max} (vapour phase, 130°C) 1628m, 1441s, 1389sh, 1374vs, 1280w, 1264m, 1208vs, 1095vs, 1067sh, 1019vs, 962m, 737vs,br, 673vs, 601sh, 587s, 536m, 468s and 417br; (nujol mull) 1630s, nujol, 1279m, 1200vs, 1089vs, 1020sh, 1011vs, 847w, 735vs,br, 671vs, 585vs, 545sh, 539sh, 528vs, 525sh, 458s, 412m, 345w, 300m and 249s cm^{-1}. The compound was soluble in benzene, hexane and carbon tetrachloride, and appeared stable to atmospheric oxidation but sensitive to moisture. The infrared spectrum of a sample of the vapour contaminated by moist air showed extra bands characteristic of acetoxime.

Reaction of trimethylindium with acetoxime

Trimethylindium (2·7 gm., 16·9 m mole) in toluene was allowed to react at -78°C with acetoxime (1·23 gm., 16·9 m mole) in hexane (30 ml.) in a double Schlenk tube with evolution of methane. Solvent was removed under vacuum, leaving a white solid which after vacuum sublimation/distillation was identified as dimeric dimethyl(isopropylideneaminoxy)indium, $(Me_2C:NOInMe_2)_2$, m.pt 57°C. [Found: C, 27·8; H, 5·5; In 52·7%; M (cryoscopic in benzene), 483. $C_{10}H_{24}In_2N_2O_2$ requires C, 27·6; H, 5·5; In, 52·9%; M, 434]. ν_{max} (nujol mull), 1612m, nujol, 1366vs, 1269sh, 1261m, 1156m, 1076vs, 1064sh, 1005sh, 985vs, 952s, 927s, 810w, 704vs, 646s, 646s, 631sh, 564w,br, 524s, 510s, 473m. cm^{-1}; (benzene solution), 429sh, 392s, 323w, and 255m,br, cm^{-1}. The compound was soluble in such solvents as benzene, hexane and carbon tetrachloride, and was only slowly affected by dry air, but was more sensitive to moisture than its gallium analogue.

Reaction of trimethylthallium with acetoxime

Trimethylthallium (1·72 gm., 6·9 m mole) in ether (10 c.c.) was mixed with acetoxime (0·504 gm., 6·9 m mole) in hexane (20 c.c.) in a double Schlenk tube at room temperature. Methane evolution was essentially complete after two minutes, during which time the solution became warm.

The product was obtained as well formed needles after removal of some of the solvent, and was identified as dimethyl(isopropylideneaminoxy)thallium, $(Me_2C{:}NOTlMe_2)_n$, m.p. 124°. (Found: C, 19•6; H, 3•7; 71, 66•4%. $C_5H_{12}NOTl$ requires C, 19•6; H,3•9; 71, 66•7%). ν_{max} (nujol mull) 1595w, nujol, 1359s, 1253s, 1170w, 1161w, 1054vs, 966vs, 946sh, 930vs, 810sh, 791vs, 632vs, 540s. cm^{-1}.

The compound was insoluble in carbon tetrachloride and hexane, and only very slightly soluble in benzene. It was soluble in ether, from which it could conveniently be crystallised, and very soluble in water, in which it was hydrolysed to acetoxime and dimethylthallium hydroxide. Crystals suffered only slight surface decomposition during prolonged exposure to moist air.

Reaction of methyl-lithium with acetoxime

A solution of acetoxime (3•51 gm., 50 m mole) in diethyl ether (20 c.c.) was added by suringe to a solution of methyl-lithium (1•175 gm., 50•4 m moles) in diethyl ether (50 c.c.) in a double Schlenk tube at room temperature. The resulting vigorous reaction with evolution of methane caused the ether to boil, and isopropylideneaminoxylithium, $(Me_2C{:}NOLi)_n$, was simultaneously precipitated. The product was purified by washing with ether. (Found: C, 45•5; H, 7•1; Li 8•8%. C_3H_6LiNO requires C, 45•6; H, 7•6; Li, 8•8%). It did not melt when heated to 350°, and was insoluble in the common organic solvents, but dissolved in water to form lithium hydroxide and acetoxime.

DISCUSSION

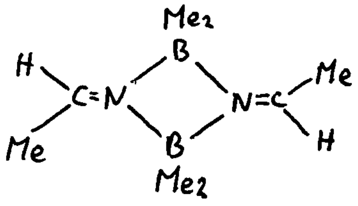
Hydroboration reactions of Methyl Cyanide

The first publication about the methyl cyanide-diborane system was in 1942 when Schlesinger and Burg[68] reported the formation of a solid adduct $MeCN,BH_3$ from diborane and methyl cyanide. Its dissociation at room temperature into the gaseous reactants was accompanied by slight decomposition to an involatile liquid which was not identified. Burg[69] later suggested that two hydrogen atoms shifted from the boron atom to the carbon of the cyanide group forming an N-substituted borazine, but he gave no supporting evidence. The proposed mechanism involved step-wise transfer of hydrogen across the cyanide group, giving the possibility of isolating an alkylideneaminoboron intermediate.

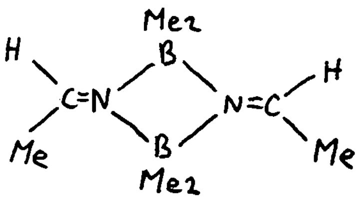
$$RCN,BH_3 \longrightarrow [RCH{:}NBH_2]_n \longrightarrow (RCH_2NBH)_3$$

The formation of N-triethylborazine $Et_3N_3B_3H_3$ from the controlled decomposition of the methyl cyanide-diborane adduct was confirmed by Emeleus and Wade[70] who also demonstrated a further example of the reaction by isolating N-tri-n-propylborazine from the decomposition of the ethyl cyanide-diborane adduct. During the course of this work, a very small quantity of a volatile material was detected spectroscopically, and identified tentatively as the azomethine intermediate $(MeCH{:}NBH_2)_n$. The infrared spectrum of this material showed a band at 1685 cm^{-1} which is in the region expected for bands due to C=N stretching vibrations, and two intense bands in the 2400 cm^{-1} region which were assigned to $B\text{-}H_2$ stretching modes.

Experiments were then carried out to determine whether or not stable alkylideneamino could in fact be prepared.[30] The method chosen was to select as acceptor molecule a compound in which only one hydrogen atom was attached to boron, the remaining two valencies being occupied by unreactive groups, thus allowing only one hydrogen transfer stage: $MeCN, BHR_2 \longrightarrow (MeCH{:}NBR_2)_n$. Trimethyl- and triethylboron were found not to react with methyl cyanide at temperatures up to 100°C and consequently alkyl groups were used as the unreactive groups. The reaction between tetramethyldiborane and methyl cyanide gave dimeric ethylideneaminodimethylboron $(MeCH{:}NBMe_2)_2$. Two isomers of this compound, a liquid and a solid, were isolated and nuclear magnetic resonance spectral evidence was presented supporting cis- and trans- structures for them.



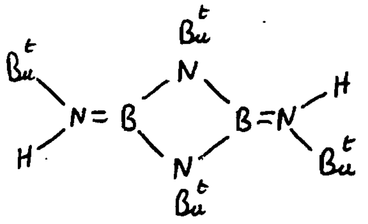
Trans-isomer



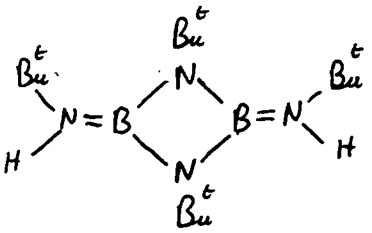
Cis-isomer

An X-ray crystal structure determination has confirmed the <u>trans</u> structure for the solid isomer. Ref 7.

Lappert and Majumdar[71] obtained spectroscopic evidence for a similar type of isomerism involving a four-membered boron-nitrogen ring with exocyclic double bonds to born atoms in the compound 1,3-di-t-butyl-2,4-di-t-butylamino-1,3-diaza-2,4-boretane, but no isomers were separated



Trans-isomer



Cis-isomer.

Meanwhile, Hawthorne[72] had shown that it was unnecessary to start with a dialkylborane, R_2BH in order to prepare stable alkylideneaminoboranes; reaction of trimethylamine-t-butylborane, Me_3N,BH_2Bu^t, with various nitriles, RCN, afforded stable alkylideneamino-t-butylboranes $(RCH:NBHBu^t)_2$. He commented on the possibilities of cis-trans isomerism but was unable to separate his products into geometrical isomers, presumably because his choice of reactants, with only one alkyl group per boron, led to too many opportunities for isomerism.

The reactions of diborane with trifluoroacetonitrile and trichloroacetonitrile have been studied recently.[73] It was found that the vapour phase reaction at room temperature was very slow, but a rapid reaction giving borazines and polymeric products was observed at 90-100°C.

$$6\ CF_3CN + 3B_2H_6 \longrightarrow 2\ (CF_3CH_2)_3N_3B_3H_3.$$

Diborane and trichloroacetonitrile exploded when heated in a sealed tube, but when the reaction was carried out in tetrahydrofuran or dimethoxyethane as solvent the intermediate trichloroethylideneaminoborane could be isolated:

$$2nCCl_3CN + nB_2H_6 \longrightarrow 2\ (CCl_3CH{:}NBH_2)_n.$$

The molecular weight was not reported. When the reaction was carried out at a higher temperature, the corresponding borazine, $(CCl_3CH_2)_3N_3B_3H_3$ was obtained.

During this present work, a new investigation into the reaction between methyl cyanide and diborane has been carried out in order to establish the following points:

1. Can this reaction be adapted into a convenient preparative route to N-triethyl borazine?
2. Can the "volatile material" [suggested by Emeleus and Wade to be $(MeCH{=}NBH_2)_n$] be prepared on a reasonable scale, and what is its identity?
3. What is the nature of the non-volatile products of the reaction?

Other boron hydride derivatives have been used as potential hydroboration agents, and their reactions with methyl cyanide studied.

Reaction of Methyl Cyanide with Diborane

When a preformed sample of the methyl cyanide-diborane adduct is heated, the hydroboration reaction is so violent as to cause extensive explosive decomposition, with formation of intractable polymers and hydrogen. In order to avoid this hazard, the adduct must decompose as it is formed, and so, diborane diluted with nitrogen was passed into methyl cyanide in a solvent at a temperature at which the adduct would immediately rearrange without complete breakdown of the products. This becomes an attractive preparative route to N-triethyl borazine. The preparation was eventually attempted on a molar scale, in order to prepare sufficient quantities of the volatile material for its isolation. The temperature chosen for the reaction was 80°C and this was maintained by a water bath. The solvent, benzene initially, was found to be unnecessary and in later experiments, diborane was passed into refluxing methyl cyanide.

The N-triethyl borazine is probably most easily obtained from the reaction mixture by distillation at atmosphere pressure followed by fractionational distillation of the distillate. Pumping the volatile reaction products onto the vacuum line followed by a vacuum line fractionation always led to samples of N-triethyl borazine contaminated by more volatile impurities. Hydrolysis of these samples with strong alkali gave hydrogen, ethylamine and ammonia, demonstrating the presence of N-H impurities. When a slight deficiency of diborane is used, some of the volatile impurities do not seem to be formed. The removal of the excess methyl cyanide presents no problem and this method gives initially a cleaner sample of the borazine. The yields of N-triethyl borazine were poor and the best yield obtained was about 35-40%. The advantage of this preparation is that relatively large quantities of the borazine, about 25 grams, may be prepared in one experiment in a matter of two or three days. The largest scale attempted was molar but there appears to be no reason why the scale of the experiment should not be increased further provided due care is exercised to control the temperature and rate of passage of diborane.

Characterisation of the "Volatile Material".[x]

The largest quantity of this material obtained in any one experiment was 0·4 gm. In the early stages of purification, the compound was found to contain varying quantities of N-ethylborazines as less volatile impurities and diethyl ether as a more volatile impurity. Repeated fractionation through a trap maintained at -96°C effectively removed all the ether. This could easily be seen in the vapour phase infrared spectrum, where trace quantities of the very volatile ether showed up strongly in the region $\sim$ 1150 cm^{-1}. The purest sample obtained after repeated fractionation through a trap maintained at -46°C still contained a fairly high proportion of ethylborazines, and these were seen in the ^1H nuclear magnetic resonance spectra of the sample. The extreme air sensitivity of the compound, (trace quantities sometimes gave a green flash on exposure to air when the infrared gas cell was removed from the vacuum line), and the tiny quantities in which

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[x] Fraction III in Experimental Section, Page

it was formed rendered techniques other than vacuum line techniques extremely difficult for its purification. Consequently, since a pure sample was never obtained in a large enough quantity, analytical figures were of no great value, so physical methods were used almost exclusively for its identification. The compound was finally identified as diethylaminodiborane[74] $Et_2NB_2H_5$ by the following physical methods.

(a) Infrared Spectra.

The vapour phase infrared spectra of samples of the volatile material were taken immediately after each fractionation during the purification, and the fractionation procedure was repeated until successive spectra were identical, with respect to the relative intensities of the peaks. At this stage, it was assumed that the spectrum recorded was that of either an essentially pure compound, or a mixture whose composition could no longer be changed by further fractional distillation. The most striking features of the spectra were the two sharp, intense peaks at about 2500 cm^{-1}, which had previously been assigned to BH_2 stretching modes, the peak at 1635 cm^{-1} suggested to be a C=N stretching mode, and a series of very intense peaks in the region 950-1450 cm^{-1}.

The infrared evidence together with the n.m.r. evidence outlined below indicates that the material may be $Et_2NB_2H_5$ or $EtNHB_2H_5$.

A comparison of the infrared spectrum of the unknown material with that of an authentic sample of diethylaminodiborane showed the two materials to be identical.

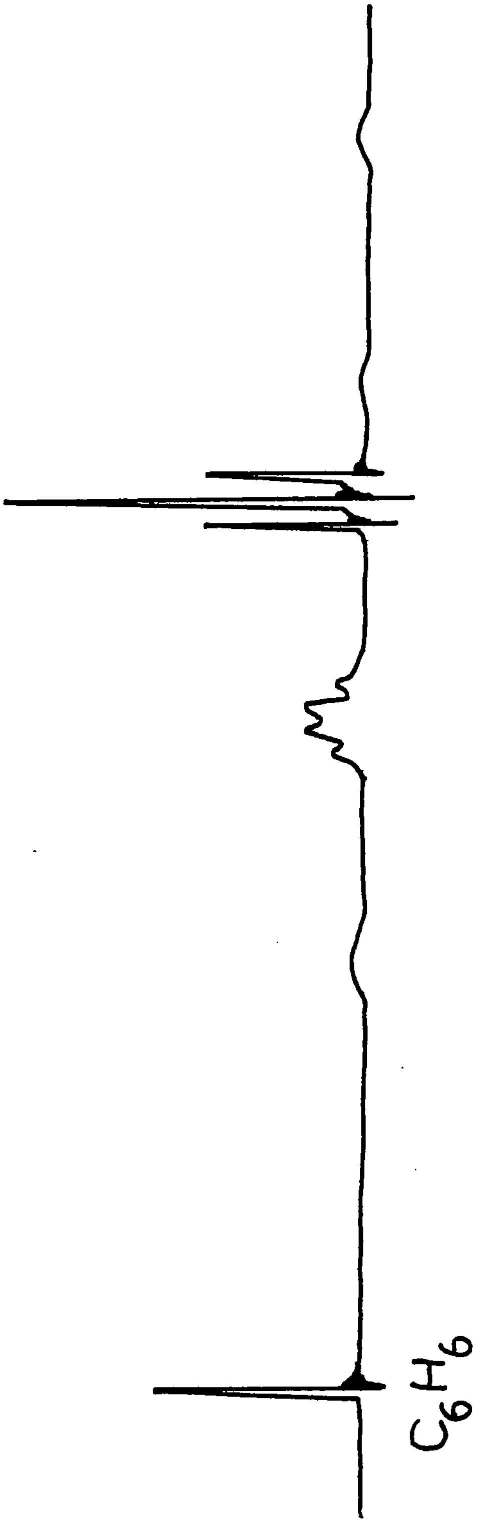
A complete vibrational assignment of the infrared and Raman spectra of dimethylaminodiborane $Me_2NB_2H_5$ has been made[75] and Table VIII shows the assignments proposed, for some of the peaks in the infrared spectrum of diethylaminodiborane $Et_2NB_2H_5$. Where there is good correlation, the frequencies for the corresponding peaks in the infrared spectrum of ethylaminodiborane $EtNHB_2H_5$ are also listed. The peak at 1634 cm^{-1} in the infrared spectrum of the volatile material thought to arise from a C=N stretching mode can now be assigned with reasonable certainty to a stretching vibration of the bridging hydrogen, corresponding to the band at 1604 cm^{-1} in the infrared spectrum of diborane.[76]

(b) Nuclear Magnetic Resonance Spectra

The proton magnetic resonance spectrum was recorded in benzene solution, with tetramethylsilane as internal reference, as is shown in Fig. II. The spectrum consisted of two quartets (τ= 7•2 and 8•5 with J = 7•2 c.p.s. and 127 c.p.s. respectively) and a triplet (τ = 8•9, with J = 7•2 c.p.s.), complicated by another quartet and triplet of much lower intensity from the borazine impurity. The quartet with J = 127 c.p.s. was assigned to a proton bound to one boron atom, the spin of which is 3/2. The other quartet and the triplet were assigned to the methylene and methyl protons of an ethyl group.

The integrated spectrum did not distinguish conclusively between ethyl- and diethylamino-diborane, because:

FIGURE II



^1H n.m.r. spectrum of $Et_2NB_2H_5$.

TABLE VIII

$Et_2NB_2H_5$	$EtNHB_2H_5$	$Me_2NB_2H_5$	Assignment
3373			
2985vs	2976s		νCH
2950			νCH
2899	2903m		νCH
2541vs	2538vs	2547	νBH_2
2478vs	2475vs	2476	νBH_2
2404			
2370			
1880	1905m	1868	$\nu BH'$
1634vs	1635vs	1635	$\nu BH'$
1555	1572m		
1449vs	1422s	1458	δCH
1387m			
1305			
1193vs	1183vs	1198	δBH_2
1133m			
1067vs	1053vs	1063	νBN
953vs	946vs	956	νCN
891		896	pBH_2
792	795m		
715	717m		

(a) the peaks due to the B-H protons were very broad, thus making them of uncertain intensity.

(b) the coupling constant was so large that only one component of the quartet could be integrated at a time, and so further reduced the intensity of the B-H proton.

(c) other components of the quartet were partially obscured by the ethyl group protons, and

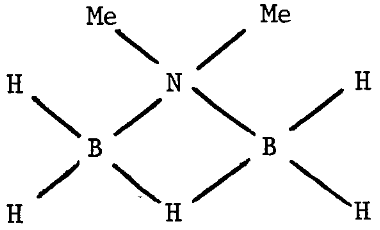
(d) the N-triethylborazine impurity also coincided with the ethyl group protons, thus increasing their intensities even further.

The proton magnetic resonance spectrum of an authentic sample of ethylaminodiborane was recorded. It was similar to that of diethylaminodiborane except that it was impossible to resolve completely the peak due to the methylene of the ethyl group into a quartet.

The "B nuclear magnetic resonance spectrum, was recorded in benzene solution, with methyl borate as external reference. A triplet of doublets was obtainef 36·8 p.p.m. to high field of methyl borate with J(triplet) = 130 c.p.s., and J(doublet) = 31 c.p.s. Boron-proton coupling has been observed only when the proton is bonded directly to the boron atom.[79] The spin of a proton is 1/2, and so the triplet of doublets is best interpreted as coupling of a single boron atom with two protons in one environment giving the triplet and with one proton, in a different environment, splitting each component of the triplet into a doublet.

"B n.m.r. spectrum of diethylaminodiborane.

An element of structure which fulfils these conditions is found in the aminodiboranes, where the terminal protons give rise to the triplet and



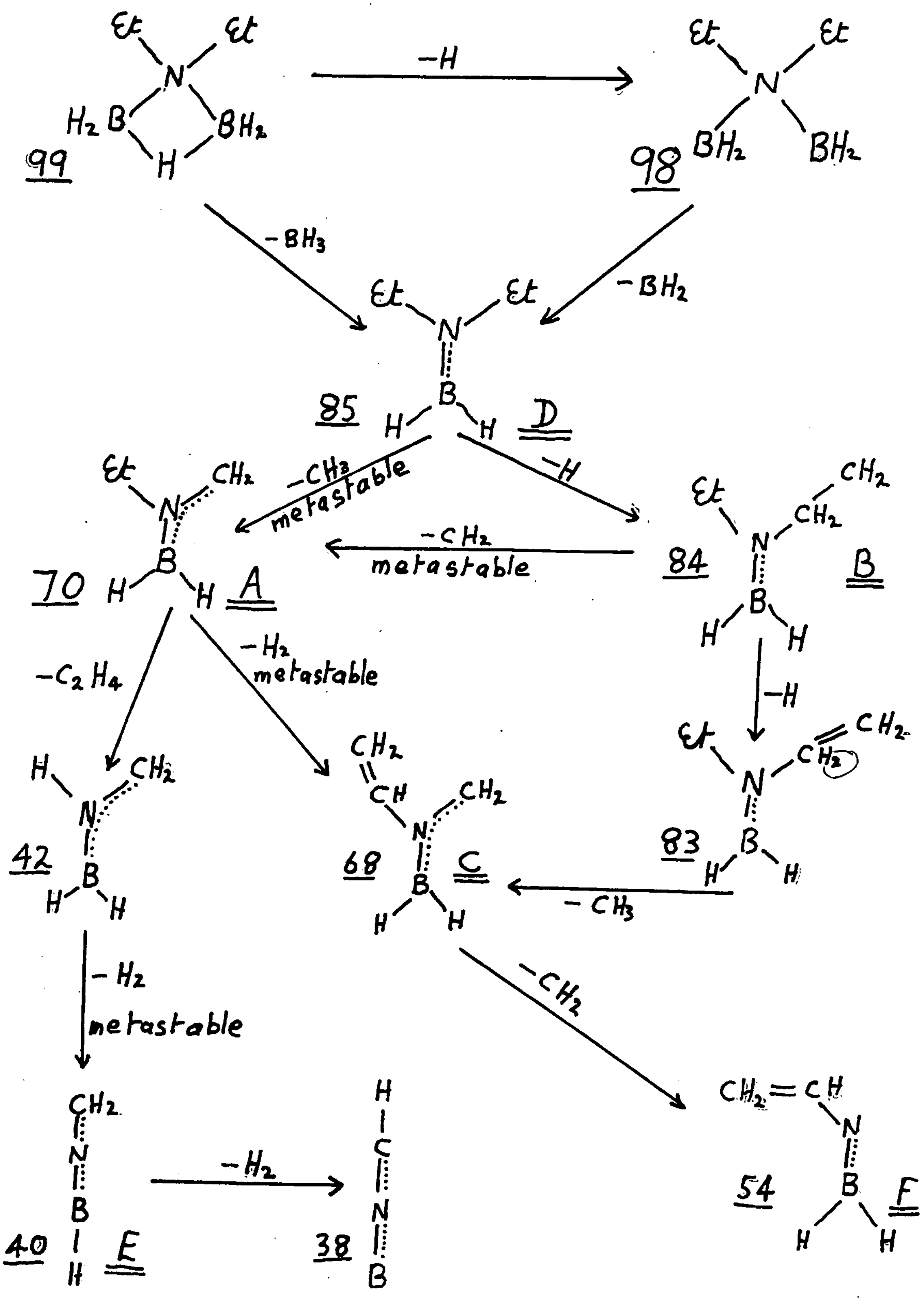
the bridging proton gives rise to the doublet, providing there is no rapid exchange of protons. The "B nuclear magnetic resonance spectrum of dimethylaminodiborane $Me_2NB_2H_5$ has been published[77] and also is a triplet of doublets with J(triplet) = 130 c.p.c. and J(doublet) = 30 c.p.s. More recent work on the "B nuclear magnetic resonance spectra of aminodiboranes[78] shows the fine structure to be dependent upon temperature.

At -39°C, the spectrum is a well-defined triplet of doublets, but at 83°C, this breaks down into a simple sextet showing that proton exchange is rapid and that each boron atom is equally coupled to all five protons. In the limit of rapid exchange, the sextet becomes perfectly symmetrical, and this is the case when the spectrum is recorded in an ether solvent, at room temperature.

(c) Mass Spectra

The mass spectrum was recorded and accurate masses measured on the major peaks and on the peaks at high mass. Some of the high mass peaks were shown to be B_3N_3 fragments derived from ethylborazines. The highest mass peak which could not be attributed to a fragment from an ethylborazine was at mass 98, and the accurate mass of this peak corresponded to diethylaminodiborane with the bridging hydrogen knocked off. The major peaks, and their empirical formulae are listed in Table V on page 36 in the experimental section. The interpretation of the breakdown pattern is best shown in diagrammatic form; (see following page). The integral masses are shown on the left of the structure thus 99, and the intensities of the peaks are shown in decreasing intensity thus A B etc. "Metastable" means that the mechanism is confirmed by the presence of a metastable ion.

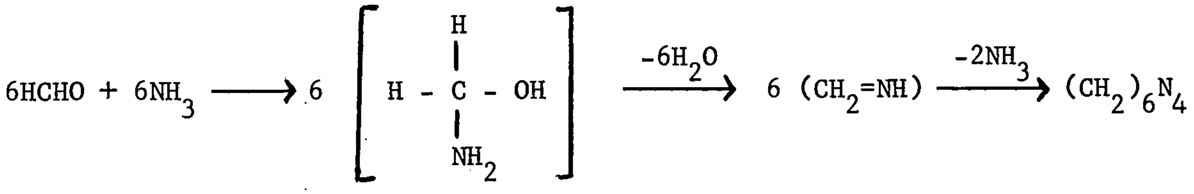
The breakdown pattern is consistent with the formulation of the compound as $C_4H_{15}B_2N$, and was found to be identical with that of an authentic sample of diethylamino diborane.


99
-H
98
-BH3
-BH2
85
D
-CH3 metastable
-H
70
A
-CH2 metastable
84
B
-C2H4
-H2 metastable
-H
42
68
C
83
-CH3
-CH2
-H2 metastable
40
E
-H2
38
54
F

The most intense peak in the spectrum is at mass 70. This fragment has the formula C_3H_9BN and the structure assigned, $[CH_2\overset{---}{-}NEt\overset{---}{-}BH_2]^+$, is analogous to an allyl cation, $[CH_2\overset{---}{-}CEt\overset{---}{-}CH_2]^+$. A related structure is suggested for the peak at mass 42 ($[CH_2\overset{---}{-}NH\overset{---}{-}BH_2]^+$), while the structure proposed for the ion of mass 68, $[CH_2\overset{---}{-}N(vinyl)\overset{---}{-}BH_2]$ combines the allyl and butadiene structural types. The peaks at masses 40 and 38 seem to rise from cations related to allene cations, and extended unsaturation is seen to be a feature of the structures proposed for some of the other fragments. The major uncertainty in these assignments is the position of the hydrogens, and studies on the mass spectrum of $Et_2NB_2D_5$ are planned to check these assignments.

The unusual observation which has emerged from this reaction is that reduction of a compound containing two carbon atoms attached to one nitrogen has produced a compound containing four carbon atoms attached to one nitrogen atom. This may be compared with the following reactions:-

(a) The formation of hexamethylene-tetramine from formaldehyde and ammonia which is thought to go by the following intermediates:



$$6HCHO + 6NH_3 \longrightarrow 6\left[\begin{array}{c} H \\ | \\ H - C - OH \\ | \\ NH_2 \end{array}\right] \xrightarrow{-6H_2O} 6\ (CH_2{=}NH) \xrightarrow{-2NH_3} (CH_2)_6N_4$$

(b) The reaction of tertiary butyl cyanide with tertiary butyl magnesium chloride:

$$Me_3CC{\equiv}N + Bu^tMgCl \xrightarrow[\text{12 hrs. then hydrolyse}]{150^\circ C} \underset{10\%}{Me_3CCHO} + \underset{31\%}{Me_3CCH{=}NCH_2CMe_3}$$

(c) The reaction of diethylaluminium hydride with phenyl cyanide:[79]

$$Et_2AlH \text{ or } Bu^i_2\,AlH + PhCN \xrightarrow{\text{hydrolyse}} PhCHO + \underset{\text{(small quantity)}}{PhCH{:}NCH_2Ph}$$

(d) The pyrolysis of phenyl(bis)isobutylaminoboron.[80] $(Bu^iNH)_2BPh$:

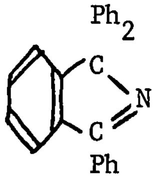
$$(Bu^iNH)_2BPh \longrightarrow Bu^iNH_2 + Bu^i_3N_3B_3Ph_3 + C_8H_{17}N$$

The fragment $C_8H_{17}N$ was identified by its mass spectrum and may be $Me_2CHCH{=}NBu^t$ or $Me_2C{=}CHNHBu^i$.

(e) The reaction of triethylboron with diphenyl ketimine.[81]

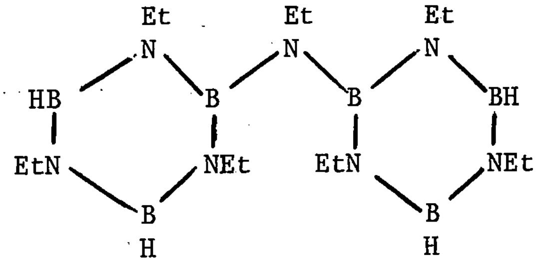
$$Ph_2C{=}NH + Et_3B \longrightarrow C_2H_4 + Ph_2C{=}N - CHPh_2$$

+ some



Characterisation of the involatile material, Fraction V from the hydroboration of methyl cyanide.

When all the materials volatile at room temperature had been pumped away, a viscous oily residue remained. A colourless liquid distilled from this at 60°C and 0·01 Hg. pressure and this liquid had analytical figures corresponding to $Et_7N_7B_6H_4$ for which a formula can be drawn based on two N-triethylborazine units linked through an NEt bridge (see diagram) but the



molecular weight, obtained cryoscopically in benzene, was about 270, instead of the required 372. It was thought that this low answer may have been due to some N-triethylborazine and some N-H impurities in the sample, so attempts were made to prepare authentic samples of the compound, $Et_7N_7B_6H_4$. The first method attempted was the hydroboration of methyl cyanide with N-triethylborazine because, if this worked, it furnished a ready explanation for the formation of $Et_7N_7B_6H_4$ during the reaction of methyl cyanide with diborane.

i.e. $2\ Et_3N_3B_3H_3 + N \equiv CMe \longrightarrow (Et_3N_3B_3H_2)_2\ NCH_2Me$

There was no reaction under the conditions used. The second method attempted was the reaction between ethylamine and N-triethylborazine.

i.e. $2\ Et_3N_3B_3H_3 + EtNH_2 \longrightarrow (Et_3N_3B_3H_2)_2\ NEt + 2H_2$

In this case, reaction did occur to some extent, but not in the ratio 1:2, $EtNH_2:Et_3N_3B_3H_3$, as was hoped for. The reaction product was a mixture of N-ethylaminoborazines with some linked borazine rings, and every fraction obtained had a very strong, sharp infrared absorption due to the N-H stretching mode.

The mass spectrum of Fraction V was recorded, and the most intense series of peaks were observed around mass 245. Higher mass peaks were observed in groups around masses 295 and 325, with some very weak peaks around masses 295 and 325. The accurate masses of some of the peaks indicates that the B:N ratio is less than 1:1, and this excess of nitrogen in this fraction is not surprising if a disproportionation reaction is responsible for the formation of diethylaminodiborane. Further work on the mass spectrum of this fraction is necessary before any speculation can be made about its true identify; it seems possible that the fraction still contains various components, and that the analytical and molecular weight figures represent average values.

Reaction of Chloroboranes with Methyl Cyanide

Boron trichloride and diborane equilibrate rapidly in the presence of ethers to give chloroborane etherates.[82]

$$B_2H_6 + BCl_3 + 3\ R_2O \longrightarrow 3\ H_2BCl.\ OR_2$$

$$B_2H_6 + 4\ BCl_3 + 6\ R_2O \longrightarrow 6\ HBCl_2.OR_2$$

These chloroborane etherates react with carbonyl compounds, reducing them to alcohols.

The reactions of $HBCl_2.OEt_2$ and $H_2BCl.OEt_2$ with methyl cyanide were studied in the expectation that ethylideneaminoboron dichloride and B-trichloro-N-triethylborazine would be formed.

$$nBHCl_2 + nMeCN \longrightarrow (MeCH{=}NBCl_2)_n$$

$$3\ BH_2Cl + 3MeCN \longrightarrow Et_3N_3B_3Cl_3.$$

In neither case was the desired product obtained. Both reactions appeared to go via a disproportionation into methyl cyanide-boron trichloride adduct $MeCN,BCl_3$, with the simultaneous formation of borazines and borazine polymers. No volatile material other than $MeCN,BCl_3$ was obtained from the monochloroborane reaction. The infrared spectrum of the residue demonstrated the presence of B-H, C≡N and C=N groups and this was partly confirmed by the evolution of hydrogen, ammonia and ethylamine on alkaline hydrolysis. The reaction of dichloroborane with methyl cyanide resulted in the formation of larger quantities of $MeCN,BCl_3$ and this time, a liquid could be distilled from the residue. Analysis of this liquid showed it to be a mixture of N ethyl-B chloro-borazines, and this conclusion was supported by very broad intense absorptions in the infrared spectrum at ~ 1450 cm^{-1}, which is in the region characteristic of borazine ring vibrations.

The reactions of chloro-alane-amine adducts[83], e.g. $HAlCl_2,NMe_3$ and gallium halide hydrides $HGaCl_2$, $HGaBr_2$[84] with methyl cyanide have been studied. These reactions also appear to involve a disproportionation and the desired alkylideneamino derivatives are not obtained. The reaction products are yellow involatile glues.

Reaction of Organoaluminium Compounds with Aliphatic Cyanides.

Reactions between cyanides and organoaluminium compounds have been studied by several groups of workers, who have shown that ketones, aldehydes, or amines may be obtained by hydrolysis of the reaction mixture. For example, Gilman and Marple[50] obtained phenyl p-tolyl ketone in 17% yield from phenyl cyanide and tri-p-tolylaluminium at about 130-140°:

$$\begin{tikzcd} \mathrm{PhCN} + (\mathrm{p\text{-}MeC_6H_4})_3\mathrm{Al} \arrow[r] & {[\mathrm{p.MeC_6H_4.C(Ph) = NAl\ (p\text{-}Me.C_6H_4)_2}]} \arrow[d, "\mathrm{H_2O}"] \\ & \mathrm{p.Me.C_6H_4.COPh} \end{tikzcd}$$

Acetophenone has been prepared in 26-39% yield from phenyl cyanide using methylaluminium dichloride at 170°C and in 48-60% yield using dimethylaluminium chloride.[15,16]

The higher alkyls of aluminium tend to lose olefin when heated with nitriles; subsequent transfer of hydrogen affords an aldehyde or amine on hydrolysis.[85]

$$\begin{tikzcd} \mathrm{PhCN} \arrow[r, "\mathrm{Bu_3^iAl}\ 80\text{-}90^{\circ}", "(-\mathrm{C_4H_8})"'] & {[\mathrm{PhCH{:}N.AlBu_2^i}]} \arrow[r, "\mathrm{Bu_3^iAl}", "(-\mathrm{C_4H_8})"'] \arrow[d, "\mathrm{H_2O}"] & {[\mathrm{PhCH_2N(AlBu_2^i)_2}]} \arrow[d, "\mathrm{H_2O}"] \\ & \mathrm{PhCHO} & \mathrm{PhCH_2NH_2} \end{tikzcd}$$

Dibutylaluminium hydride $\mathrm{Bu_2AlH}$, reacts similarly.[85,14,79] Vacuum distillation of a mixture of propyl cyanide and $\mathrm{Bu_2AlH}$ was reported to give n-butylidene aminodibutyl aluminium, $(\mathrm{Pr.CH{=}NAlBu_2})_n$, the molecular weight of which was not recorded.[14]

Work on the phenyl cyanide-triphenylaluminium system has shown that a crystalline solid adduct, $PhCN,AlPh_3$, can be prepared by direct reaction of the components in benzene solution.[86] This rearranges slowly at 90° and more rapidly at 140°C to form $(Ph_2C{=}NAlPh_2)_n$, m.pt. 298-300°C, for which ebullioscopic measurements on benzene solutions indicate a degree of association n=1·1 - 1·2.[52]

The reactions of phenyl cyanide with Me_3Al, Et_3Al, Ph_3Al, Me_2AlCl and Me_2AlH have been studied,[38] by Dr. J. E. Lloyd of this Department. All react exothermically with phenyl cyanide at room temperature, the first four forming adducts $PhC{\equiv}N,AlR_3$ which rearrange when heated into dimeric alkylideneaminoaluminium derivatives, $(PhCR{=}NAlR_2)_2$. The hydride Me_2AlH forms $(PhCH{=}N,AlMe_2)_2$ directly, no adduct being isolable at room temperature.

Dr. Lloyd also initiated an investigation into the reactions between methyl cyanide and organoaluminium compounds. The author completed this investigation and subsequently studied the reactions between tertiary butyl cyanide and organoaluminium compounds. The discussion in the following pages concerns both of these reaction systems.

Alkyl Cyanide Adducts

The adducts and their rearrangement reactions are listed in Table IX. The compounds $RCN,AlMe_3$ (R = Me, Et, or Bu^t), $R'CN,AlEt_3$, and $R'CN,AlMe_2Cl$(R' = Me or Bu^t) were readily prepared by the exothermic reaction between equimolar quantities of nitrile and organoaluminium. The triphenylaluminium complexes $R'CN,AlPh_3$ were prepared from the ether complex $Et_2O,AlPh_3$ and only a slight excess of nitrile, a reaction that may reflect

TABLE IX.

Thermal rearrangement of adducts RCN,AlR'_3

Adduct	Decomposition		Non-polymeric product	Yield (%)
	Temp.	Reaction [+]		
$Bu^tCN,AlMe_3$	150°	Me →	$(Bu^tCMe:N{\cdot}AlMe_2)_2$	95
$Bu^tCN,AlEt_3$	155-160	C_2H_4,↑H →	$(Bu^tCH:N{\cdot}AlEt_2)_2$	80
$Bu^tCN,AlPh_3$	170	Ph →	$(Bu^tCPh:N{\cdot}AlPh_2)_2$	85
$Bu^tCN,AlMe_2Cl$	240	Me →	$(Bu^tCMe:N{\cdot}AlMeCl)_2$	60
$Bu^TCN,AlMe_2H$[x]	<20	H →	$(Bu^tCH:N{\cdot}AlMe_2)_2$	90
$MeCN,AlMe_3$	120-150	MeH,↑Me →	$(Me_2C:N{\cdot}AlMe_2)_2$	15-20
$MeCN,AlEt_3$	110-130	EtH,↑Et →	$(MeCEt:N{\cdot}AlEt_2)_2$	18
$MeCN,AlPh_3$	190-200	PhH,↑Ph →	$(MeCPh:N{\cdot}AlPh_2)_n$	15
$MeCN,AlMe_2Cl$	160-165	MeH,↑Me →	$(Me_2C:N{\cdot}AlMeCl)_2$	7
			+	
			$(Me_2C:N{\cdot}AlMeCl)_n$	4
$MeCN,AlMe_2H$[x]	<20	H →	$(MeCH:N{\cdot}AlMe_2)_2$	90
$EtCN,AlMe_3$	160-170	MeH,↑Me →	$(EtCMe:N{\cdot}AlMe_2)_2$	26

[x] Adduct itself not isolated, rearranging below room temperature. [+] In this column, ↑ indicates gas evolved, → indicates group or atom migrating.

the relative volatilities of the two competing donor molecules rather than their relative donor strengths, as Mole has shown that in deuterochloroform solution phenyl cyanide only partly displaces co-ordinated ether from triphenylaluminium.[86] Alkyl cyanide adducts of dimethylaluminium hydride RCN,$AlMe_2H$ were not isolated; like the phenyl cyanide compound these rearranged rapidly at room temperature to give the products described below.

The alkyl cyanide adducts isolated decomposed rapidly in the presence of air or moisture, but were readily characterised by the methods outlined in the Experimental Section. They were monomeric in benzene, and their infrared spectra contained bands characteristic of co-ordinated nitrile groups at frequencies some 30-60 $cm.^{-1}$ higher than the frequency of the free nitrile, as shown in Table X. An increase in the frequency, $\Delta\nu$, associated with the C≡N stretching vibration on co-ordination is a familiar feature of the spectra of nitrile adducts. It has generally been attributed to[87,88,89] the mechanical constraint imposed on the vibration of the nitrogen in the linear adducts compared with the free nitrile, although an actual strengthening of the C=N bond on coordination has also been suggested.[90] Both explanations require $\Delta\nu$ to increase with the strength of the coordinate link. However, recent calculations by Beattie and Gilson[91] of C≡N and B-N stretching frequencies for adducts MeCN,BX_3 (X=F,Cl, or Br) have shown the need for caution in relating $\Delta\nu$ to Lewis acidity in nitrile adducts because of 'mixing' of the various vibrational modes. Recent force constant determinations and molecular orbital calculations have been reported by Purcell and Drago.[92] It was found that the C≡N frequency increased only slightly as a result of kinematic coupling in the subsystem [C≡N $\longrightarrow$ acid]. However, the C≡N force constant was shown to increase significantly upon coordination of acetonitrile and is the main cause for the frequency increase. The molecular orbital calculations supported this, and allowed the conclusion that the N_{2s} orbital in overlapping more with the C_{2s} and $C_{2p\sigma}$ orbitals was responsible for the observed strengthening of the C≡N link upon coordination of CH_3CN to Lewis acids.

In our alkyl cyanide adducts, the increase, $\Delta\nu$, in the nitrile stretching frequency on co-ordination varies with the acceptor molecule,

TABLE X

Infrared spectroscopic results for adducts $RC{:}N,AlR'_3$

			Acceptor molecule			
	Nitrile	-	$AlPh_3$	$AlEt_3$	$AlMe_3$	$AlMe_2Cl$
νCN	PhCN	2230^{x}	2265^{+}	2270^{x}	2273^{+}	$2273^{\ddagger}$
	MeCN	2253^{x}	2287^{+}	2290^{x}	2296^{+}	2296^{+}
	Bu^tCN	2235^{x}	2285^{+}	2282^{x}	2282^{+}	2293^{+}
$\Delta\nu$	PhCN	-	35	40	43	43
	MeCN	-	34	37	43	43
	Bu^tCN	-	50	47	47	58
νAlN	PhCN	-	411^{+}	394^{x}	391^{+}	$412^{\ddagger}$
	MeCN	-	408^{+}	4402^{x}	401^{+}	412^{+}
	Bu^tCN	-	$424^{\ddagger}$	412^{x}	$412^{\ddagger}$	$407^{\ddagger}$

Values for $EtCN,AlMe_3$; $\nu CN = 2294^{x}$. $\Delta\nu = 47$. Frequencies in $cm.^{-1}$.

^{x}Liquid film. $^{+}$ Nujol mull. ‡ Benzene solution.

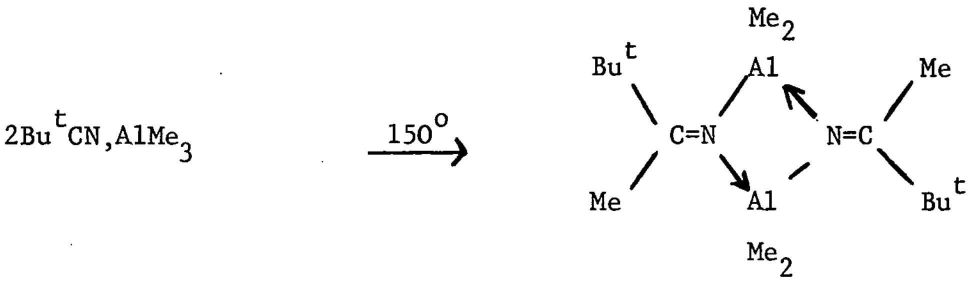
and follows a similar trend to that observed for related phenyl cyanide adducts. Values of $\Delta\nu$ for methyl cyanide complexes do not, in fact, differ significantly from the values for corresponding phenyl cyanide compounds, and can be interpreted in terms of increasing acceptor power $AlPh_3 < AlEt_3 < AlMe_3 = AlMe_2Cl$. In studies of nitrile complexes of inorganic halides, other workers have found that values of $\Delta\nu$ for complexes of phenyl cyanide were significantly lower than values for complexes of methyl cyanide.[81,88] This result was explained in terms of interaction between ring and nitrile orbitals in the phenyl cyanide adducts, allowing contribution from such canonical forms as $^{+}C_6H_5{=}C{=}N^{-}$. The values obtained for $\Delta\nu$ for the complexes of t-butyl cyanide are still higher than the values for the complexes of the other nitriles, and correspond to the series of increasing acceptor power $AlEt_3 = AlMe_3 < AlPh_3 < AlMe_2Cl$. As the frequency differences involved are small, too much significance should not be attached to their values, although the results are in general agreement with the sequence that would be expected from consideration of the relative electronegativities of the groups attached to aluminium.

A recent publication[93] about the structure and infrared spectra of complexes of organoaluminium compounds with nitriles is generally in good agreement with the work reported here.

Also listed in Table X are the frequencies of bands that are considered to be associated with the Al-N stretching vibration. A sharp band in the region 390-425 $cm.^{-1}$ is common to the spectra of all the adducts, but is absent from the spectra of the component nitriles and organoaluminium acceptor compounds. A band associated with the Al-N stretching vibration might be expected in this region by analogy with related compounds such as aminealuminium hydride adducts[94] and amino-aluminium alkyls[95] in the spectra of which bands near 500 cm.$^{-1}$ have been assigned to Al-N vibrations. Also, the spectrum of the gallium trichloride complex MeCN,GaCl$_3$ contains a band at 335 cm.$^{-1}$, which has been calculated to arise largely from a Ga-N stretching vibration[91,96]. The extent to which the band near 400 cm.$^{-1}$ in the spectra of the organoaluminium-nitrile adducts may be regarded as due to an Al-N stretching vibration, however, is uncertain. Beattie and Gilson have recently shown that, in the spectrum of $(Me_3N)_2AlH_3$, a band near 200 cm.$^{-1}$ is more properly that designated ν_{Al-N}, the band at 460 cm.$^{-1}$ being mainly associated with deformation of the trimethylamine groups[91,96]. Thus, although an Al-N stretching vibration is considered to be involved in the vibration giving rise to the absorption near 400 cm.$^{-1}$ in the spectra of our nitrile complexes, it is not possible to draw any detailed conclusions from the precise value of the frequency of this band. Although the spectra of several of the nitrile complexes were recorded up to 200 cm.$^{-1}$, no other band attributable to ν_{Al-N} was found.

Rearrangement Reactions

These are summarised in Table IX. The adducts of t-butyl cyanide rearranged in a similar manner to those of phenyl cyanide, forming dimeric alkyl-ideneaminoalanes in good yield, e.g.,



The adduct of triethylaluminium lost ethylene at about 155-160°, and subsequent (or simultaneous) hydrogen transfer gave $(Bu^tCH{:}N{\cdot}AlEt_2)_2$ the neopentylideneamino-compound. Triethylaluminium itself loses ethylene[40,97] at about 160°, although by the reversible reaction $Et_3Al \rightleftharpoons Et_2AlH + C_2H_4$, so that the overall rate of decomposition appears slower than the irreversible decomposition of the triethylaluminium-nitrile adducts. When $Bu^tCN,AlEt_3$ was held at about 160°, some transfer of ethyl apparently occurred as well, the product having an extra band in the C:N region of the infrared spectrum at 1626 $cm.^{-1}$, the frequency at which such a band might be expected for the compound $(Bu^tCEt{:}N{\cdot}AlEt_2)_2$, but a pure sample of the latter was not isolated. It was found convenient to use a slightly higher temperature for the rearrangement of the triphenylaluminium adduct, although there seemed little difference between the migratory aptitudes of methyl and phenyl groups. However, the methyl groups of $Bu^tCN,AlMe_2Cl$ were markedly less mobile, a temperature of 240° being necessary for the rearrangement of this adduct. Other workers also have found the transfer of organic groups from alkylaluminium halides to occur less readily than the transfer of groups from the trialkyls.[15,16] Hydrogen transfer occurred much more readily than alkyl or or aryl transfer; dimethylaluminium hydride and t-butyl cyanide gave neopentylideneaminodimethylaluminium dimer when mixed at, or below, room temperature. Our results show that the readiness with which groups attached to aluminium migrate to the carbon of a cyanide group decrease in the sequence H (of $AlMe_2H$) $\gg$ Me (of $AlMe_3$) $\simeq$ Et (of $AlEt_3$) > Ph (of $AlPh_3$) > Me (of $AlMe_2Cl$), a sequence in which there appears to be decreasing negative charge on the migrating atom or group.

The possibility of further rearrangement of the alkylideneamino-derivatives, involving transfer of another organic group from aluminium to the carbon of the azomethine group, e.g. $(Bu^tCR{:}N{\cdot}AlR_2)_2 \longrightarrow (Bu^tCR_2N{\cdot}AlR)_n{}^m$ was explored by heating the methyl compound $(Bu^tCMe{:}N{\cdot}AlMe_2)_2$ to 280°, but little change occurred. There appeared to be no reaction, either, when this compound was heated with trimethylaluminium to a similar temperature, conversion into $Bu^tCMe_2N(AlMe_2)_2$ then being considered possible.

Methyl and ethyl cyanide differ from t-butyl and phenyl cyanides in having attached to the α-carbon atom hydrogen atoms that allow the possibility of acidic reaction. As a consequence, the thermal decomposition of their adducts with organoaluminium compounds follows a different course, the main reaction involving cleavage of organic groups from aluminium, e.g.

$$nCH_3CN,AlR_3 \longrightarrow (R_2AlCH_2CN)_n + nRH$$

Similar cleavage of organic groups from magnesium occurs in reactions between Grignard reagents and certain alkyl cyanides.[3] Thus, methane was evolved from methylaluminium adducts, ethane from the ethylaluminium compound and benzene from the phenyl compound when these were heated to the temperatures shown in Table IX. Once decomposition had started, very rapid evolution of gas occurred as the heat evolved raised the reaction temperature, so that generally the bulk of a sample of adduct was converted into a glue or glass within a minute; not all of a sample decomposed in this manner, however. The quantity of gas evolved was rarely more than 60% of that expected from the equation above, and small samples (20%) of alkylideneamino-compounds $(MeCR{:}N{\cdot}AlR_2)_n$ were recovered from the residue by vacuum sublimation, showing that a rearrangement reaction like that which occurs with phenyl or t-butyl cyanide adducts had also taken place, e.g.

$$MeCN,AlMe_3 \longrightarrow 15\text{-}20\%\ (Me_2C{:}N{\cdot}AlMe_2)_2$$

The decomposition temperature of methyl cyanide adducts is lower than that of corresponding adducts of t-butyl or phenyl cyanides, although the triphenylaluminium compound is comparatively stable to heat, and the adduct of dimethylaluminium chloride loses methane less readily than that of trimethylaluminium. A consequence of the lower reaction temperature is that the slight rearrangement of $MeCN,AlEt_3$, which occurs simultaneously with the loss of ethane, involves migration of ethyl groups rather than loss of ethylene and migration of hydrogen. Migration of hydrogen occurs when methyl cyanide and dimethylaluminium hydride are mixed at, or below, room temperature, so that in this system methyl cyanide does not differ from the other cyanides studied.

The involatile glassy residues left after methyl cyanide adducts have decomposed, shown as $(R_2AlCH_2CN)_n$ above, are apparently complex polymeric materials. They are insoluble in the common inert organic solvents, but are readily hydrolysed by dilute acids. Values of the R:Al ratio lie between 1:1 and 2:1, showing that some rearrangement as well as cleavage of groups R from aluminium has occurred, a conclusion supported by the presence of ketones in the hydrolysate and by bands characgeristic of C=N groups as well as C≡N groups in the infrared spectra of the polymers.

Although adducts RCN,AlR'_3 do not rearrange appreciably at temperatures below 100°, Reinheckel and Hahnke[16] have shown that addition across the C⋮N link occurs at a lower temperature if the adduct is treated with an equimolar quantity of the organoaluminium compound:

$$RCN,AlR'_3 + AlR'_3 \longrightarrow \frac{1}{n}\ (RR'C{:}N{\cdot}AlR'_2)_n + AlR'_3$$

If the product is hydrolysed, this reaction affords a route to ketones RR'CO, which might otherwise be obtained in only very low yield (if R contains hydrogen attached to the α-carbon atom), or not at all (if R' = Et, when loss of ethylene and hydrogen migration tend to occur). As a route to rearranged compounds $(RR'C{:}N{\cdot}AlR'_2)_n$ it is less useful, since the product contains combined AlR'_3, possibly in the form $RR'C{:}N(AlR'_2) \longrightarrow AlR'_3$. Thus we found that rearrangement, apparently to $Me_2C{:}N(AlMe_2)AlMe_3$, was essentially complete after a 1:2 mixture of methyl cyanide and trimethylaluminium had been heated in benzene to 80° for 1 day, but the product, a viscous oil, retained trimethylaluminium tenaciously under vacuum and attempts to isolate the isopropylideneamino-compound $(Me_2C{:}N{\cdot}AlMe_2)_2$ from it were unsuccessful.

When a mixture of methyl cyanide and dimethylaluminium hydride was heated at 145° for 30 minutes, appreciable addition across the C:N *double* bond occurred. Hydrolysis of the residual glue gave mainly methane and ethylamine and only small quantities of hydrogen and ammonia:

$$MeCN \xrightarrow[<20^{\circ}]{Me_2AlH} \frac{1}{n}\ (MeCH{:}N{\cdot}AlMe_2)_n \xrightarrow[145^{\circ}]{Me_2AlH} \frac{1}{m}\ [MeCH_2N(AlMe_2)_2]_m$$

Partial reduction beyond the azomethine stage has already been observed in other reactions between a nitrile and an excess of an organometallic compound. For example, benzylamine is among the products when benzonitrile is treated with an excess of dibutyl-aluminium hydride[79] or tributylaluminium[85] (acting as a source of the hydride Bu_2AlH) and the reaction mixture is hydrolysed, while neopentylamine is formed in a similar reaction sequence involving t-butyl cyanide and the Grignard reagent[6] Bu^tMgCl at 150°;

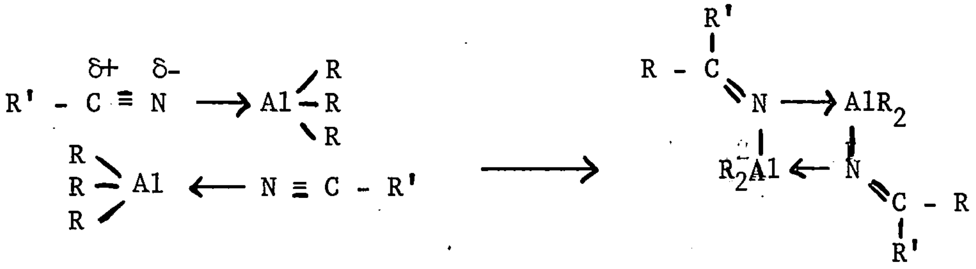
$$\begin{tikzcd}
Me_3C{\cdot}CN \arrow[r, "Me_2CMgCl", "-CH_2{:}CMe_2"'] & {[Me_3C{\cdot}CH{:}NMgCl]} \arrow[d, "hydrolysis"] \arrow[r, "Me_2CMgCl", "-CH_2{:}CMe_2"'] & {[Me_3C{\cdot}CH_2{\cdot}N(MgCl)_2]} \arrow[d, "hydrolysis"] \\
 & Me_3C{\cdot}CHO & Me_3C{\cdot}CH_2{\cdot}NH_2
\end{tikzcd}$$

It should be stressed that in such reactions an *excess* of the organometallic compound is needed, as only one of the groups originally attached to aluminium appears to be available for reaction. This may be contrasted with the behaviour of aluminium hydride itself, in which *two* hydrogen atoms per aluminium are available for transfer reactions, e.g.[36]

$$MeCN + Et_3N,AlH_3 \text{ ——— } [MeCH{:}N{\bullet}AlH_2] \text{ ——— } [MeCH_2NAlH]$$

Two of the four hydrogen atoms of lithium aluminium hydride are similarly available for the reduction of nitriles to amines, although reaction can be stopped at the azomethine stage.[98,99]

A plausible mechanism for the rearrangement of these nitrile adducts involves nucleophilic attack by the migrating group on the carbon of the nitrile:



The observation already noted that the rearrangement occurs less readily if electronic charge is withdrawn from the migrating group is consistent with this.

Recent kinetic studies by Pasynkiewicz and Kuran[100] on the reaction of phenyl cyanide with trimethylaluminium in molar ratio 1:1 at 120°, show it to be of first order, implying an intramolecular, rather than an intermolecular rearrangement of the complex. More studies[101] by the same authors on the reaction of phenyl cyanide with trimethylaluminium in molar ratio 1:2 show it to be of second order kinetics and to be much faster than the 1:1 molar ratio reaction thus confirming our own work and that of Reinheckel and Jahnke[16].

Further rearrangement of the alkylideneaminoalanes themselves could involve a similar mechanism, nucleophilic attack on the carbon of the azomethine group by the migrating group, and will therefore occur less readily, because of the increased steric hindrance about that carbon atom, because of the lower effective positive charge on it, and because of the greater withdrawal of electrons grom the groups R' attached to aluminium now that two nitrogen atoms are also attached to aluminium. The lack of further rearrangement of $(Bu^tCMe:N{\cdot}AlMe_2)_2$ at about 280° or of attack by Me_3Al on this compound, contrasted with the reaction between $(MeCH:N{\cdot}AlMe_2)_2$ and $AlMe_2H$ at 145°, are all consistent with this interpretation of the factors influencing these reactions. The alkylideneamino-compounds, however, are also susceptible to nucleophilic attack at the aluminium atoms, which can expand their coordination number above four. Those prepared in this work, although less sensitive to air and moisture than the adducts, still required manipulation in an atmosphere of nitrogen. The sensitivity was found to be least for those compounds that had most crowding of the groups about the aluminium atoms, the compound $(Bu^tCMe:N{\cdot}AlMe_2)_2$, for example, being hydrolysed too slowly by dilute acid to enable this method to be used for its analysis. All these aluminium compounds were much more readily hydrolysed than the related ethylideneaminoboranes, $(MeCH:N{\cdot}BR_2)_2$, in which the boron, already four-co-ordinate, cannot accommodate further donor molecules.[30]

The strong tendency of HAl groups to add across nitriles prompted the study of the reaction between dimethylaluminium hydride and hydrogen cyanide in hexane at -78° as a route to $(H_2C:N{\cdot}AlMe_2)_n$. Hydrogen was evolved, however, and tetrameric dimethylaluminium cyanide, $(Me_2AlCN)_4$, was produced. This compound has previously been prepared from trimethylaluminium and hydrogen cyanide.[67]

Features of the infrared spectra of the alkylideneamino- and benzylideneaminoaluminium derivatives are given in Table XI. All the spectra contain strong or very strong absorption bands in the region 1600-1675 cm.$^{-1}$ characteristic of the C:N stretching vibration, the frequency apparently being sensitive to the groups attached to the carbon, being highest for compounds with hydrogen or a small alkyl group attached to this carbon atom and lowest when t-butyl or phenyl groups are the substituent.

The infrared spectra of some ketimines has been studied,[102] and frequencies of the C=N stretching vibrations reported. The frequencies for ketimines is also highest when an alkyl group, and lowest when an aryl group is bonded to the carbon atom of the azomethine group.

Another common feature of the infrared spectra is a band between 437 and 478 cm.$^{-1}$, which appears to be associated with a vibration of the $(AlN)_2$ ring. A band at 508 cm.$^{-1}$ has been shown[95] to be associated with a ring vibration in the spectrum of the aminoalane $(Me_2NAlMe_2)_2$, although the sensitivity of this band to deuteration of the dimethylamino group, when it moves to 482 cm.$^{-1}$, shows that movement of the rest of the molecule contributes to this absorption. Other bands between 450 and 500 cm.$^{-1}$ in some of the spectra, particularly those of phenyl or chloro-derivatives, make assignment uncertain in these

TABLE XI

Infrared spectroscopic results for rearranged compounds $(\mathrm{RR'C:N\cdot AlR'_2})_n$

Compound	C=N stretch	Al-CH$_3$ δ(sym.)	Al-CH$_3$ stretch(asym.) + rock	Al-CH$_3$ stretch (sym.)	Al-N stretch
$(\mathrm{MeCH:M\cdot AlMe_2})_2^{*}$	1675vs	1190s	719sh,690s	560w	461s
$(\mathrm{Bu^tCH:N\cdot AlMe_2})_2^{+}$	1661vs	1192vs	730sh,689vs	580s	449m
$(\mathrm{Me_2C:N\cdot AlMe_2})_2^{\ddagger}$	1658s	1181ms	722sh,684s	554w	465m
$(\mathrm{EtCMe:N\cdot AlMe_2})_2^{\ddagger}$	1653vs	1181s	710sh,682vs	550w	465w
$(\mathrm{PhCMe:N\cdot AlMe_2})_2^{\ddagger}$	1634vs	1183s	717s,676vs	567m	478w
$(\mathrm{PhCH:N\cdot AlMe_2})_2^{+}$	1630vs	1183vs	745vs,685vs	575m	470w
$(\mathrm{Bu^tCMe:N\cdot AlMe_2})_2^{+}$	1630vs	1192s	734vs,684vs	582w	448m

Compound	C=N stretch	Al-CH$_3$ δ(sym.)	Al-CH$_3$ stretch + rock	Al-Cl stretch	Al-N stretch
$(\mathrm{Me_2C:N\cdot AlMeCl})_2^{*}$	1650vs	1192vs	737sh,699vs, 566m.	489m	454m
$(\mathrm{Bu^tCMe:N\cdot AlMeCl})_2^{\S}$	1625vs	1203s	691s, 568w	494m	467m
$(\mathrm{PhCMe:N\cdot AlMeCl})_2^{+}$	1613vs	1186s	719vs, 662vs, 573vs	477w	437m
$(\mathrm{Bu^tCH:N\cdot AlEt_2})_2^{*}$	1656vs	-	-	-	454s
$(\mathrm{EtCMe:N\cdot AlEt_2})_2^{*}$	1650vs	-	-	-	473m
$(\mathrm{PhCH:N\cdot AlEt_2})_2^{*}$	1633vs	-	-	-	468m
$(\mathrm{PhCMe:N\cdot AlPh_2})_n^{*}$	1621s	-	-	-	461s
$(\mathrm{PhCBu^t:N\cdot AlPh_2})_2^{+}$	1616vs	-	-	-	455m
$(\mathrm{Ph_2C:N\cdot AlPh_2})_n^{\ddagger}$	1620sh¶	-	-	-	456m

*Liquid film. +Nujol mull. ‡KBr disc. § $\mathrm{CCl_4}$ solution. ¶For a discussion of this assignment see ref. 38.

instances, but the frequencies listed in Table XI are those indicated by analogy with the less ambiguous methyl derivatives.

Seven of the compounds prepared contained $AlMe_2$ groups, and three others AlMeCl groups. Features of their spectra that are readily identified are also listed in Table XI. The dimethylalanes have a characteristic strong sharp band at 1181-1192 $cm.^{-1}$, due to the symmetrical deformation vibration of the methyl groups bound to aluminium, and a broad region of strong absorption around 700 $cm.^{-1}$, consisting of a strong or very strong band centred at 676-690 $cm.^{-1}$ with a shoulder or second band around 710-745 $cm.^{-1}$, which together can be attributed to $Al-CH_3$ asymmetrical stretching and rocking vibrations. A less intense peak at 550-582 $cm.^{-1}$ can be assigned to the $Al-CH_3$ symmetrical stretching vibration. These assignments are made on the basis of studies by Gray,[103] Hoffman and Schomburg[104] and Coates and his co-workers [95, 105] on various methylaluminium compounds.

The methylchloroaluminium compounds have a strong sharp band near 1190 $cm.^{-1}$ in their spectra [$Al-CH_3\delta(sym)$], and broad strong absorptions near 690 $cm.^{-1}$ and 570 $cm.^{-1}$ due to $Al-CH_3$ stretching and rocking vibrations. A band in the region 477-494 $cm.^{-1}$ can be assigned to the Al-Cl stretching vibration by analogy with Gray's assignments for methylaluminium chlorides.[103]

The proton magnetic resonance spectra (p.m.r.) of the alkylideneamino-derivatives were recorded, and τ values are listed in Table XII. Assignments were generally straightforward, and are indicated in the Table. It has previously been shown that p.m.r. spectra can be used to detect the presence of mixed isomers in such systems,[38,30] on the basis of the number of peaks corresponding to Al-Me or Al-Et groups.

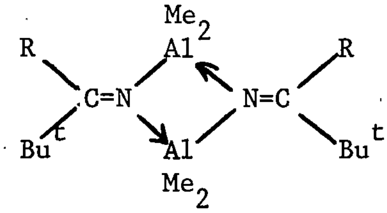
TABLE XII

Proton magnetic resonance spectroscopic results

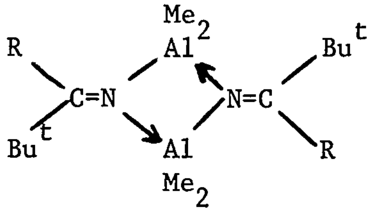
Compound	Solvent	τ values of peaks (p.p.m.; τMe$_4$Si = 10·00) =C-H	=C-Me	=C-Et or =C-Bu^t	Al-Me or Al-Et
$_2$C:N·AlMe$_2$)$_2$	CCl$_4$	-	$7\cdot9_0$s(1)	-	$10\cdot9_3$s(1)
CH:N·AlMe$_2$)$_2$	CCl$_4$	$1\cdot6_0$q(1)	$7\cdot8_9$d(3)	-	$10\cdot8_3$s; $10\cdot8_8$s; $10\cdot9_3$s(6)
CMe:N·AlMe$_2$)$_2$	CCl$_4$	-	$7\cdot9_0$s(3)	$7\cdot6_7$q(2);$8\cdot8_0$t(3)	$10\cdot9_1$s(6)
CMe:N·AlMe$_2$)$_2$	C$_6$H$_6$	-	$8\cdot2_8$s(3)	$7\cdot9_9$q(2);$9\cdot2_1$t(3)	$10\cdot4_3$s(6)
^{t}CMe:N·AlMe$_2$)$_2$	C$_6$H$_6$	-	$7\cdot8_4$s(1)	$8\cdot8_7$s(3)	$10\cdot3_4$s(2)
^{t}CH:N·AlMe$_2$)$_2$	CCl$_4$	$5\cdot3_6$s(1)	-	$8\cdot8_8$s(9)	$10\cdot8_7$s(6)
^{t}CH:N·AlMe$_2$)$_2$	C$_6$H$_6$	$4\cdot2_8$s(1)	-	$9\cdot1_4$s(9)	$10\cdot5_7$s(6)
^{t}CH:N·AlEt$_2$)$_2$	None	$1\cdot7_5$s(1)	-	$8\cdot9_1$s(9)	$8\cdot9_9$t(6);$10\cdot0_2$q(4)
$_2$C:N·AlMeCl)$_2$	CCl$_4$	-	$7\cdot7_3$c	-	$10\cdot6$c
$_2$C:N·AlMeCl)$_2$	C$_6$H$_6$	-	$8\cdot6_3$c	-	$10\cdot3_7$c
^{t}CMe:N·AlMeCl)$_2$	C$_6$H$_6$	-	$7\cdot8_5$d	$8\cdot9_7$s	$10\cdot1_6$s;$10\cdot2_4$s

ternal standard, benzene (τ = 2·73); internal standard, tetramethylsilane in all ner cases. s = singlet, d = doublet, t = triplet, q = quartet; relative tensities in parentheses.

The p.m.r. spectra of the tertiary butyl compounds, (Bu^{t}RC=NAlMe$_2$)$_2$ show only one peak attributable to AlMe$_2$ and indicate that only the <u>trans</u>-isomer was present (Structure II), unless the difference between the two types of $AlMe_2$ groups in the cis-form (Structure I) was insufficient to be detected.



Structure (I)



Structure (II)

The formation of only the trans- isomer of the compounds $(Bu^tCMe:AlMe_2)_2$ $(Bu^tCH:N{\bullet}AlMe_2)_2$, and $(Bu^tCH:N{\bullet}AlEt_2)_2$, is intelligible in that the bulk of the butyl groups might lead to bond-angle strain in a cis-isomer. The presence of only one isomer in the first two of these butyl compounds is also consistent with their crystalline form and the sharpness of their melting points. The X-ray crystal structure of $(Bu^tCMe{=}N{\bullet}AlMe_2)_2$ is shown below.

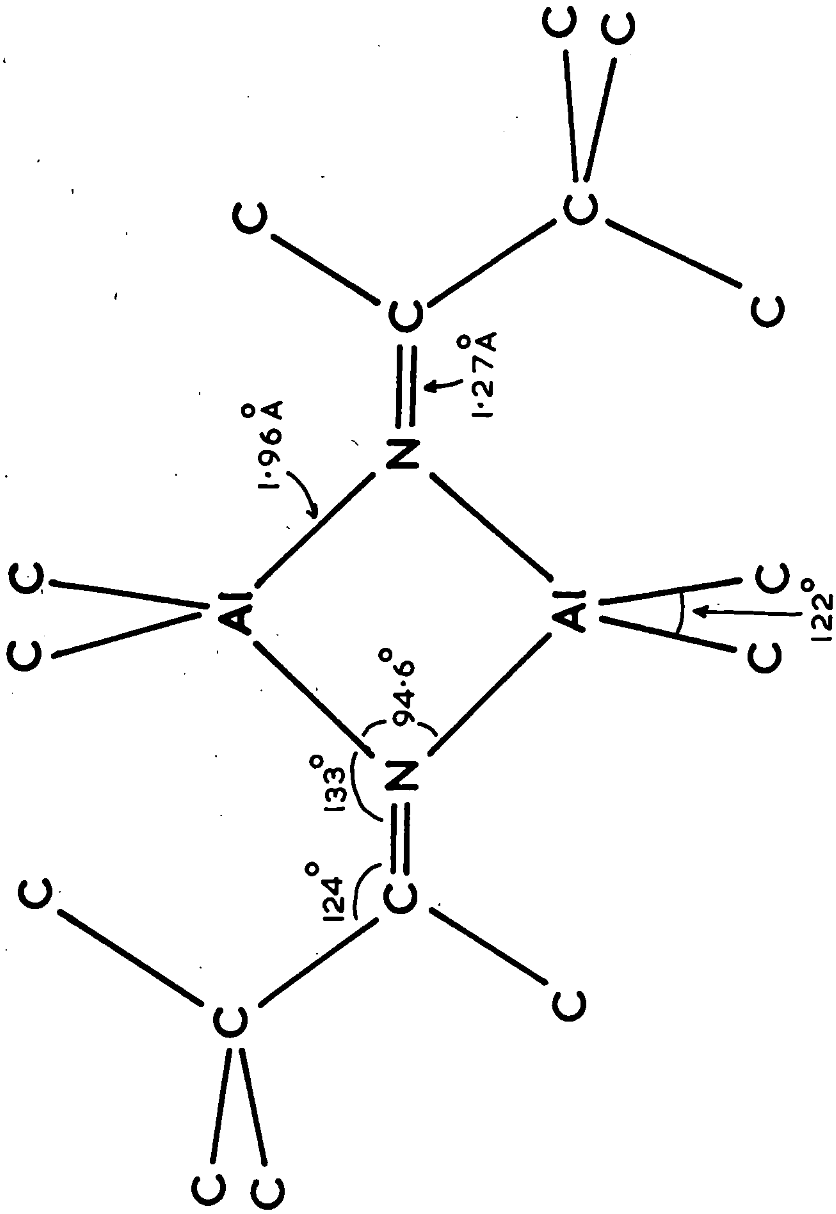
The p.m.r. spectra of both the methylchloro-compounds $(Me_2C:N{\bullet}AlMeCl)_2$ and $(Bu^tCMe:N{\bullet}AlMeCl)_2$ were recorded, but were unexpectedly complex and could not be interpreted with certainty. Their p.m.r. spectra should not be sensitive to the relative orientation of the AlMeCl groups. However, the slow development of a yellow colour in the solutions of these compounds suggested that the complexity might be due to impurities resulting from decomposition of the samples or attack on the solvent or tetramethylsilane standard. The p.m.r. spectrum of the phenyl compound $(Bu^tCPh:N{\bullet}AlPh_2)_2$ in deuterotoluene was complex and could not be assigned with certainty;

τ values of peaks were 3•07c, 3•52c, 4•27c, 9•93s p.p.m.

The alkylideneaminoalanes described here are examples of compounds in which 3-co-ordinate nitrogen atoms are present in a four-membered $(Al-N)_2$ ring, in which the bond angle strain (distortion from 120° to 90°) at the nitrogen atoms appears to be greater than in the related amino-alanes $(R_2N \cdot AlR'_2)_2$ (distortion from 109° to 90°). A trimeric form $(R_2C:N \cdot AlR'_2)_3$, which would have no distortion of the bond angles has not been detected in this work, or in the work on phenyl cyanide adducts.[38] In the amino-aluminium and -gallium compounds, considered to be dimeric in the crystal phase at room temperature, ring opening to polymeric structures occurs when they are heated, the resulting glasses softening to dimeric liquids over a short temperature interval as if melting.[95] No evidence of such a crystal ⟶ glass ⟶ liquid change was detected when certain of the alkylideneaminoalanes, for which p.m.r. spectroscopic evidence of the presence of only one isomer was available, were heated slowly to the melting point under a polarising microscope, even though the greater strain expected to be present in the alkylideneamino-compounds should make a transition to a polymeric glass more likely. One must conclude therefore, that bond-angle strain in these compounds is small.

The X-ray crystal structure of $(Bu^tCMe:N \cdot AlMe_2)_2$ has been studied in these laboratories by Dr. H. M. M. Shearer and Miss J. Willis and the results are shown in Photograph II.

PHOTOGRAPH II



The most interesting features about the structure are:

(a) the Al-N-Al angle is widened significantly from 90°.

(b) the C=N bond length is 1·27Å, identical to the C=N bond length in trans-ethylideneaminodimethylboron $(MeCH{:}NBMe_2)_2$[106] and comparable with the C=C bond length of 1·34Å in ethylene.

(c) allowance for the hydrogen atoms on the methyl groups on the aluminium and on the tertiary butyl group, shows the aluminium atom to be well shielded from nucleophilic attack, hence the remarkable air stability of this compound.

Reactions of Organogallium Compounds with Cyanides.

The organic chemistry of gallium has received little attention and most of the work in the literature is associated with Coates and his co-workers. Adducts of trimethylgallium with trimethylamine, trimethylphosphine, trimethylarsine, trimethylstibine, dimethyl ether, dimethyl sulphide, dimethyl selenide and dimethyl telluride[57] have been prepared, and the different donor strengths of the donor molecules discussed. The reactions of trimethyl-gallium with amines[107,95] and weak acids[105] have also been described, methane being evolved, and the dimethylgallium derivative $(Me_2GaX)_n$ being formed.

The only reactions of trimethylgallium with unsaturated compounds described in the literature are those with methyl cyanide and acetone,[108] and the reactions of gallium alkyls and alkyl gallium hydrides in general with olefins and acetylenes.[109]

Trimethylgallium and methyl cyanide formed a solid adduct, $MeCN,GaMe_3$, m.pt. 27°C whose vapour pressure was given by $\log_{10}P_{mm} = \frac{-2342}{T} + 8{\cdot}84$. The adduct was shown to be fully dissociated in the vapour phase at 100°C and 90 mm. Hg pressure. On cooling to room temperature, the adduct was reformed, unchanged. Trimethylgallium also formed a weakadduct with acetone, but between 50 and 90°C one molecule of methane was evolved yielding a white non-volatile product with the composition $[Me_2GaOC_3H_5]_n$. On further heating at 170°C, more methane was evolved, and an orange-red involatile solid remained.

Diethylgallium hydride was found to add readily to olefins and acetylenes with the formation of unsymmetrical gallium alkyls. On attempted distillation, these alkyls tended to disproportionate into symmetrical gallium alkyls. The reaction between gallium alkyls and olefins went either by an olefin displacement or a "growth" reaction, but much less easily than that which has been observed with aluminium alkyls. In the reaction between acetylene and triethylgallium, the acetylene reacted as a weak acid and cleaved one of the gallium-carbon bonds, with the spontaneous evolution of ethane.

$$Et_3Ga + HC{\equiv}CH \longrightarrow C_2H_6 + (Et_2GaC{\equiv}CH)_n$$

Trialkylgallium-Cyanide Adducts $R_3Ga,N{\equiv}CR'$

The adducts and their attempted thermal decomposition reactions are listed in Table XIII. The adducts were prepared by the reaction between equimolar quantities of cyanide and the organogallium compound. Trimethylgallium was measured out as a gas, in a calibrated bulb on the vacuum line. Triethylgallium was measured out by syringe, as were the cyanides themselves.

The cyanide adducts were air and moisture sensitive, but were not as reactive as their aluminium counterparts. Their infrared spectra contained bands characteristic of co-ordinated nitrile groups at frequencies some 25-35 cm.$^{-1}$ higher than the frequency of the free nitrile, as shown in Table XIV, which also compares the C≡N stretching frequency of the organogallium-cyanide adducts with the corresponding organoaluminium-cyanide adducts.

Table XIII

Thermal decomposition of adducts RCN,GaR'_3.

Adduct	Decomposition		Product
	Temp.	Reaction[x]	
$MeCN,GaMe_3$	145°C	$MeH\uparrow$	$(Me_2GaNC_2H_2)_n$
$Bu^tCN,GaMe_3$	150°C	none	$Bu^tCN,GaMe_3$
$Bu^tCN,GaEt_3$	158°C	$C_2H_4\uparrow$, $H\rightarrow$	$(Et_2GaN{=}CHBu^t)_2$
$PhCN,GaMe_3$	118°C	Polymerisation of cyanide.	$(PhCN)_3 + Me_3Ga$.
$PhCN,GaEt_3$	158°C	$C_2H_4\uparrow$, $H\rightarrow$	$(Et_2GaN{=}CHPh)_2$
$CCl_3CN,GaMe_3$	r.t.	Alkyl-halogen exchange.	Mixture containing readily hydrolysable chloride.

[x] In this column, $\uparrow$ indicates gas evolved, $\rightarrow$ indicates atom migrating.

Table XIV

Infrared spectroscopic results for adducts
$RC{:}N,MR'_3$

			Acceptor Molecule			
	Nitrile	-	$GaMe_3$	$GaEt_3$	$AlMe_3$	$AlEt_3$
$\nu C{\equiv}N$	PhCN	2230	2260	2258	2273	2270
	MeCN	2253	2285	2279	2296	2290
	Bu^tCN	2235	2266	2268	2282	2282
$\Delta\nu$	PhCN	-	30	28	43	40
	MeCN	-	32	26	43	37
	Bu^tCN	-	31	33	47	47

The values for $\Delta\nu$ are substantially less for the organogallium-cyanide adducts than for the organo-aluminium-cyanide adducts, implying that aluminium alkyls are stronger Lewis acids than gallium alkyls. Boron alkyls are completely immiscible with cyanides, so the following sequence in decreasing Lewis acid strength may be drawn up:-

$$R_3Al > R_3Ga > R_3B.$$

No consistent band was found which could be assigned with any certainty to the gallium-nitrogen stretching mode, but a complete investigation into the region beyond 400 cm.$^{-1}$ was not undertaken.

Thermal decomposition reactions.

These are summarised in Table XIII. Alkyl group migration was not observed in any of the adducts studied. The adduct of trimethylgallium with tertiary butyl cyanide dissociated on heating to 150°C, and the reactants could be recovered unchanged, even when a 2:1 excess of trimethylgallium was used. Since the reaction of trimethyl-aluminium with cyanides in molar ratio 2:1 goes at a much lower temperature than the 1:1 reaction, it seems likely that it is necessary for one molecule of the organometallic compound to be coordinated with the cyanide to increase the polarity and hence reactivity of the cyanide bond. The trimethylgallium is not co-ordinated to the cyanide at the temperature at which rearrangement would occur, and so the reaction using excess trimethylgallium does not go.

The potential acidity of methyl cyanide, in having hydrogen atoms α- to the carbon atom of the cyanide group, commented upon in the discussion of the reactions of organoaluminium compounds with cyanides, was also apparent in the reaction of trimethylgallium with methyl cyanide. No reaction took place when the adduct was heated at 120°, but at 145°C 1 mole of methane per mole of adduct was evolved, and the product was an involatile orange-red solid from which isopropylideneaminodimethylgallium $(Me_2C{=}N{\cdot}GaMe_2)_n$ could not be obtained, by attempted vacuum sublimation. The infrared spectrum of the solid showed no bands characteristic of C=N, but there was an intense absorption in the region 2150cm.$^{-1}$ This may have been due to a C≡N vibration but is more likely to have arisen from one of the $CH_2{=}C{=}N-$ stretcning modes since isocyanates, cyanates and other A=B=C systems have infrared absorptions in this region. This result is readily explained, if the methyl cyanide reacts in its 'enol' form.

$$CH_3C{\equiv}N \rightleftharpoons CH_2{=}C{=}NH$$

$$CH_2{=}C{=}NH + Me_3Ga \longrightarrow (Me_2GaN{=}C{=}CH_2)_n + CH_4$$

This residue was insoluble in all common organic solvents except acetone, in which it was extremely soluble. Acid hydrolysis of the residue gave neither acetone, nor methyl cyanide.

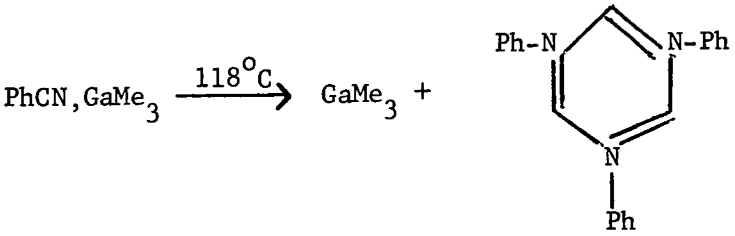
The C≡N in trichloroacetonitrile is more susceptible to nucleophilic attack than the C≡N in non-halogenated cyanides because of the inductive effect of the chlorine atoms. The adduct of trichloroacetonitrile with trimethylgallium, $CCl_3CN,GaMe_3$ slowly went brown on standing at room temperature. On warming at 70°C, the adduct went deep brown and on cooling became a viscous glue. Washing the glue with very dilute nitric acid gave a solution containing a large quantity of ionic chloride, tested by silver nitrate and nitric acid solutions, showing that some alkyl-halogen exchange had occurred. No evidence for alkyl transfer was obtained in this reaction.

The adducts of phenyl and tertiary butyl cyanides with triethylgallium slowly lost ethylene at ~160°C giving the dimeric benzylideneamino- and neopentylideneamino-derivatives respectively, $(PhCH{=}NGaEt_2)_2$ and $(Bu^tCH{=}NGaEt_2)_2$. These reactions may be compared with the corresponding reactions of triethylaluminium. The reaction analogous to the reversible thermal decomposition of triethylaluminium,

$$Et_3Al \rightleftharpoons Et_2AlH + C_2H_4$$

has not been reported for triethylgallium, but the work of Eisch[109] already mentioned leads to the conclusion that such an equilibrium reaction will occur at a temperature rather higher than that for triethylaluminium.

The pyrolysis of the phenyl cyanide-trimethylgallium adduct, $PhCN,GaMe_3$ yielded small (~5%) quantities of triphenyl triazine (kyaphenine).



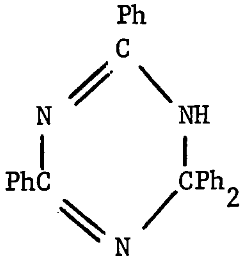
Pyrolysis of a mixture of diethyl zinc and phenyl cyanide also gives triphenyl triazine,[110] and these results have recently been confirmed in this department.[18,111]

Phenyl cyanide may be trimerised by sodium,[112,113] concentrated sulphuric acid,[114] chlorosulphuric acid,[113] iron pentacarbonyl[115] and other reagents. The trimerisation of phenyl cyanide by sodium is thought to proceed through the following initial stages:-[116]

$$PhCN + 2Na \longrightarrow PhNa + NaCN$$

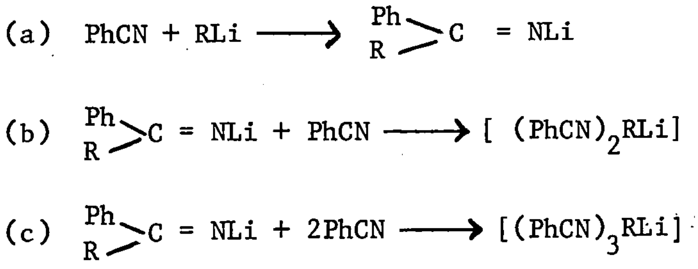
$$PhNa + PhCN \longrightarrow Ph_2C{=}NNa$$

The diphenylketimino-sodium then adds on more phenyl cyanide molecules, and trimeric species are obtained. Evidence for this sort of mechanism is obtained from the isolation of sodium cyanide and the following compound



from the reaction mixture.

Organolithium and organomagnesium compounds are also known to cause the trimerisation of phenyl cyanide,[116] when the phenyl cyanide is in large excess. The following reaction scheme has been proposed



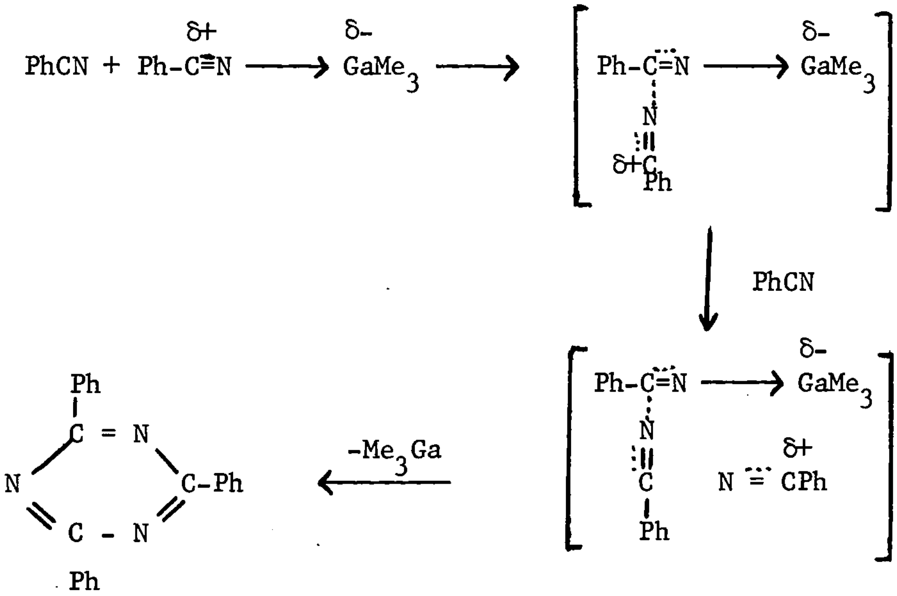
(a) $PhCN + RLi \longrightarrow \begin{matrix} Ph \\ R \end{matrix}\!\!>C = NLi$

(b) $\begin{matrix} Ph \\ R \end{matrix}\!\!>C = NLi + PhCN \longrightarrow [\,(PhCN)_2RLi]$

(c) $\begin{matrix} Ph \\ R \end{matrix}\!\!>C = NLi + 2PhCN \longrightarrow [(PhCN)_3RLi]$

There was no speculation about the structures of the intermediates in reactions (b) and (c).

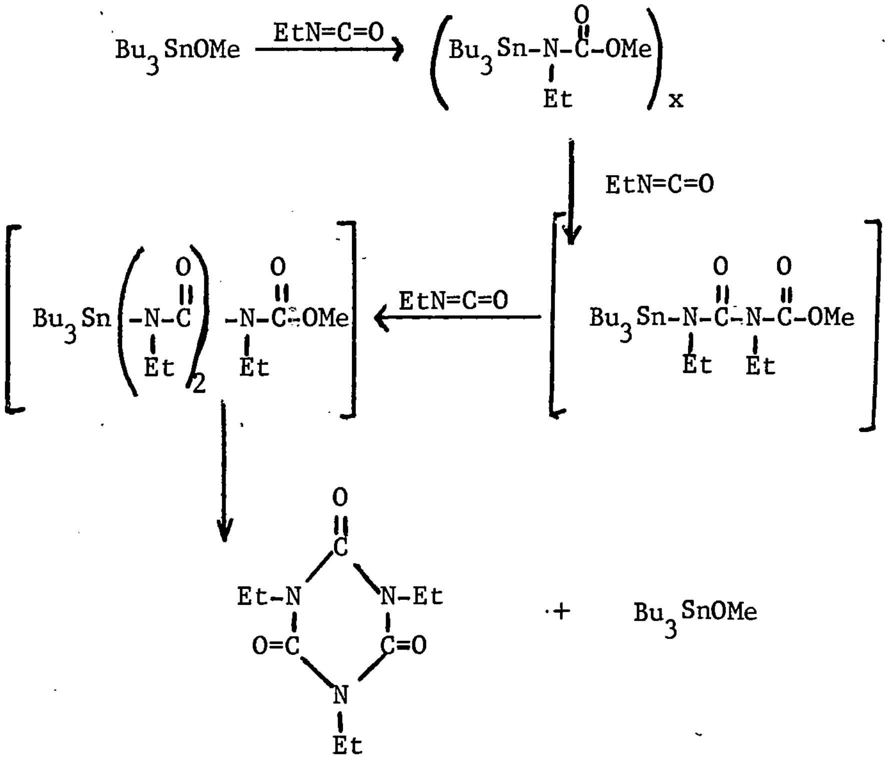
The mechanism for the trimerisation of phenyl cyanide by trimethylgallium is unknown, but it is unlikely that it occurs by the mechanism proposed above, because in no case does the methyl group of trimethylgallium add across a $C\equiv N$ bond. Co-ordination of trimethylgallium to phenyl cyanide causes a slight increase in the positive character in the carbon atom of the co-ordinated cyanide, thus making it more susceptible to mucleophilic attack.



Free phenyl cyanide itself could be a suitable nucleophile, and such a reaction mechanism as proposed above may lead to the formation of triphenyl triazine.

Alkyl and aryl cyanides can be polymerised to linear polymers by heating them with anhydrous metal chlorides.[117] The authors of this work found that the stronger the Lewis acid, (measured qualitatively by the increase in the $C\equiv N$ stretching frequency, $\Delta\nu$, upon coordination of the cyanide to the metal halide) the more difficult it was for the nitrile to polymerise, and they suggested that the reason for this behaviour was the strengthening of the C=N bond upon coordination. The temperatures necessary for polymerisation of the cyanides lay in the range 230-440°C.

The trimerisation of isocyanates by trialkyltin alkoxides[24,118] is a reaction similar in some respects to the trimerisation of phenyl cyanide. This reaction is thought to proceed by the successive insertion of N=C=O units between the tin atom and its attached group giving intermediate 1:1 "carbamate" adducts and non-isolable 1:2 and 1:3 adducts which break down into the trimer and the original tin compound.



It is unlikely that the trimerisation of phenyl cyanide by trimethylgallium goes by such a mechanism, because arylideneaminodialkylgallium derivatives have been prepared, and are stable compounds. Once formed, it seems unlikely that they would undergo further reaction. However, experiments are planned to investigate the possibility of catalysing the trimerisation of phenyl cyanide by compounds $(R_2C{=}NGaR'_2)_2$.

Reaction of Benzophenone and Ethyl Isocyanate with Trimethylgallium.

When it was found that organic cyanides were insufficiently reactive to show addition reactions with trimethylgallium, it was decided to find systems which were sufficiently reactive. Ethyl isocyanate reacted with trimethylgallium exothermically at low temperature to give the dimethylgallium derivative of N-ethylacetamide, $Me_2GaN(Et)COMe$. This apparently polymeric compound was an oil, involatile at room temperature which did not react with pyridine. Preliminary experiments on the reaction between trimethylaluminium and N-ethylacetamide, $CH_3CONHEt$, show the product to be similar to the gallium compound. Benzophenone and trimethylgallium at room temperature gave a pale green very viscous oil which slowly bubbled, under vacuum. Heating for 15 hours at 125°C gave the rearranged compound, showing that ketones are just approaching the limit of reactivity, beyond which trimethylgallium will not react with unsaturated compounds.

Reaction of Diphenylketimine with Organogallium compounds.

The reaction between diphenylketimine, $Ph_2C{=}NH$, and organogallium compounds was used as a method for the preparation of arylideneaminogallium compounds $(Ph_2C{=}NGaR_2)_2$. The reaction, evolving methane, went smoothly and quantitatively at 100^{o}C. The products from the reactions could easily be purified either by sublimation or low temperature recrystallisation, and were found to be both physically and chemically similar in properties to the alkyl and arylideneaminoaluminium compounds.

Features of the infrared spectra of the gallium compounds prepared are shown in Table XV.

Table XV.

	C=N stretch	Ga-CH$_3$ δ(sym)	GaMe$_2$ ν assym	GaMe$_2$ ν sym.	GaMe rock	GaN stretch
$(Bu^tCH{=}NGaEt_2)_2^*$	1658 cm.$^{-1}$	-	-	-	-	461 cm^{-1}
$(PhCH{=}NGaEt_2)_2$	1633 cm^{-1}	-	-	-	-	467 cm^{-1}
$(Ph_2C{=}NGaMe_2)_2$	1626 cm^{-1}	1193 cm^{-1}	570 cm^{-1}	529 cm^{-1}	742 cm^{-1}	451 cm^{-1}
$(Ph_2C{=}NGaEt_2)_2$	1613 cm^{-1}	-	-	-	-	454 cm^{-1}
$(Ph_2MeCOGaMe_2)$	-	1199 1206 cm^{-1}	586 cm^{-1}	536 cm^{-1}	751 cm^{-1}	-

*Liquid film. All others, Nujol mull.

All the spectra of the alkyl- or arylideneaminogallium compounds contain strong absorption bands in the region 1610-1660 cm.$^{-1}$ characteristic of the C=N stretching vibration. The actual figures correspond almost exactly to those of the corresponding aluminium compounds.

Another common feature of the infrared spectra is a band between 450 and 470 cm^{11} which may be associated with a vibration of the $(GaN)_2$

ring. A band at 498 cm^{-1} has been shown[95] to be associated with a ring vibration in dimethylaminodimethylgallium $(Me_2NGaMe_2)_2$. Other bands in this region in some of the spectra do tend to make this assignment rather uncertain.

Features of the infrared spectra of the methylgallium compounds that are readily identified are also shown in Table XV. These compounds have a strong sharp band at 1193-1206 cm^{-1} due to the symmetrical deformation of the methyl groups bound to gallium, a broad, very strong absorption at 742-751 cm^{-1} due to a gallium-methyl rocking mode, and absorptions at 570-586 cm^{-1} and 529-536 cm^{-1} due to the $GaMe_2$ antisymmetrical and symmetrical stretching modes respectively.

The proton magnetic resonance spectra of the rearranged compounds were recorded in carbon tetrachloride or deuterotoluene as solvent, and the τ values are listed in Table XVI.

Benzylideneaminodiethylgallium, $(PhCH{:}NGaEt_2)_2$, and neo-pentylideneaminodiethylgallium, $(Bu^tCH{:}NGaEt_2)_2$, present the opportunity for cis-, trans-, isomerism of the type commented upon on pages 95-97. This can theoretically be detected by the number of peaks corresponding to Ga-Et groups, and the nuclear magnetic resonance spectra of these compounds indicate that only the trans-isomer is present. It was almost impossible to resolve the peaks arising from the ethyl groups into a triplet and quartet. It was possible to distinguish the triplet and the quartet only by recording the integrated spectrum.

The arylideneaminogallium compounds were found to melt quite sharply, showing no crystal ⟶ glass ⟶ liquid phase transitions. As with the aluminium compounds (page 98), one must conclude once again that the bond angle strain in these compounds is small.

Table XVI

Proton magnetic resonance spectroscopic results.

τ value of peaks (p.p.m.; τ Me_4Si = 10·00)

Compound	Solvent	=CH	=CPh or Bu^t	CMe	CPh	GaMe or Et
$(PhCH{:}NGaEt_2)^{‡}$	CCl_4	1·0s	2·5c	-	-	$8{\cdot}9_7$c, $9{\cdot}5_3$c
$(Bu^tCH{:}NGaEt_2)_2^{x}$	CCl_4	$1{\cdot}8_4$s	$8{\cdot}9_3$s	-	-	$8{\cdot}9_5$c, $9{\cdot}6_3$c
$(Ph_2C{:}NGaMe_2)_2^{+}$	C_7D_8	-	$2{\cdot}2_5$c, $2{\cdot}7_5$c	-	-	$10{\cdot}22_5$
$(Ph_2C{:}NGaEt_2)_2^{+}$	C_7D_8	-	$2{\cdot}4_5$c, $2{\cdot}8_7$c	-	-	$8{\cdot}8_0$c, $9{\cdot}5_1$c
$(Ph_2MeCOGaMe_2)_2^{‡}$	CCl_4	-	-	$8{\cdot}0_2$s	$2{\cdot}7_1$c	

x Internal standard, benzene (τ = 2·73)

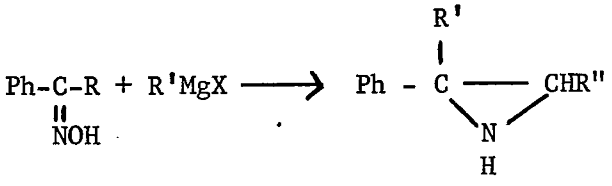
‡ Internal standard, cyclohexane (τ = 8·57)

\+ Internal standard, tetramethylsilane.

Reaction of Organometallic compounds with Acetoxime

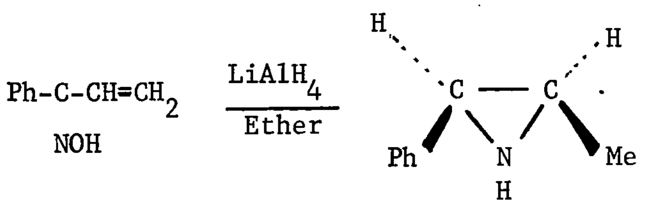
The preparation and properties of azomethine derivatives, $(R_2C{:}NMR'_2)_2$, of boron,[30] aluminium and gallium has been described in some detail. The aim in this work was the preparation of oxyazomethine derivatives, $(R_2C{:}NOMR_2)_n$, of boron, aluminium, gallium, indium and thallium. The method chosen was the reaction between acetoxime and the trimethyl derivatives of the Group III elements.

The reactions between acetoxime and some Organo-Group II compounds have received some attention.[3,122,123] Diethylzinc was found to react with acetoxime in molar ratio 1:1 to give the ethylzinc derivative, $Me_2C{=}NOZnEt$ as a colourless solid, readily crystallisable from ether. Reaction of this compound with a further mole of acetoxime gave the bis-compound, $(Me_2C{=}NO)_2Zn$, which was found to be insoluble. Recent work on this system has shown the methylzinc derivative, $Me_2C{=}NOZnMe$ to be tetrameric in benzene solution. Grignard reagents react similarly, but under some conditions, ethyleneimines can be obtained upon hydrolysis of the reaction product.[124] This reaction may be compared with the reaction



R=Me or Et R" = H or Me

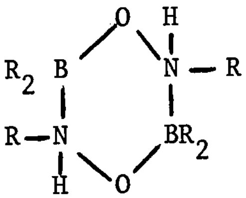
between lithium aluminium hydride and phenyl vinyl ketoxime:-[125]



cis-2-methyl-3-phenylaziridine

The dimeric acetoxime derivatives $(Me_2C{:}NOMMe_2)_2$ contain the M-O-N unit, and these are thought to exist as a six membered $(MON)_2$ ring. Several other compounds containing the "MON" unit, where M is generally boron have been described.

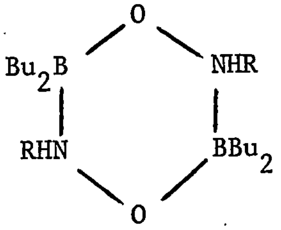
The first reports of this type of compound were by Inatome and Kuhn[34] and by Brois,[126] who described the reaction of nitric oxide with trialkylboranes. (See page 8). One of the hydrolysis products were a dimeric "BON" compound.



The same compounds have been prepared by the reaction of borinic acids with hydroxylamines,[127,128] and they were shown to be dimeric in methyl

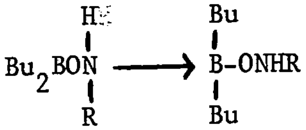
$$RNHOH + nBu_2OH \xrightarrow{EtOH} (nBu_2BONHR)_2.$$

cyanide solution (0·05 molar, Mechrolab Osmometer). Two structures were considered possible:-



I

or

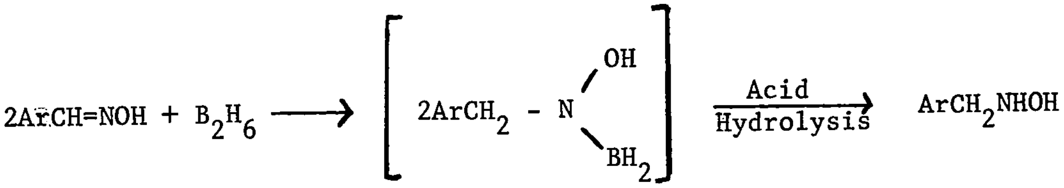


II

Structure II would have two infrared active NH stretching modes, one characteristic of three co-ordinate and the other characteristic of four-coordinate nitrogen. Structure I would only have a single infrared active NH stretching mode, at a frequency characteristic of four-coordinate nitrogen. The infrared spectrum of the reaction product shows only one absorption which can be assigned to the NH stretch, and this is at a frequency characteristic to that of four-coordinate nitrogen, and so Structure I is proposed for these "BON-BON" compounds. The reaction between di-n-butyl borinic acid and di-N-n-butyl hydroxylamine yields a

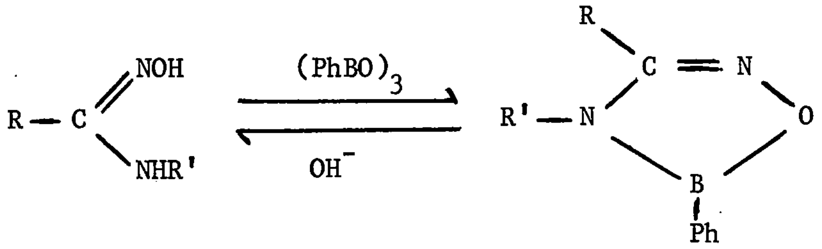
$$nBu_2BOH + nBu_2NOH \longrightarrow nBu_2BONBu_2$$

monomeric product, association apparently being prevented by the bulk of the n-butyl groups. Related compounds seem to have been formed during the reduction of aryl aldoximes by diborane in tetrahydrofuran.[129] And hydrolysis of the intermediate compound (which was not isolated) gave an N-monosubstituted hydroxylamine.



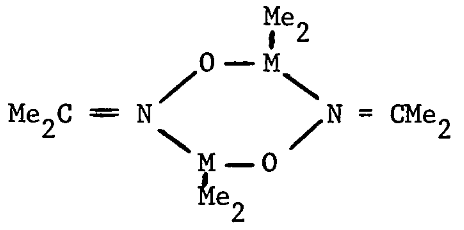
$$2ArCH{=}NOH + B_2H_6 \longrightarrow \left[2ArCH_2 - N\begin{matrix} OH \\ BH_2 \end{matrix} \right] \xrightarrow[\text{Hydrolysis}]{\text{Acid}} ArCH_2NHOH$$

Other compounds containing the "B-O-N" unit have been prepared by the reactions of boron compounds with amidoximes. Reaction of phenyl boronic anhydride with amidoximes yield, 1, 3, 5, 2-oxadiazaboroles. This reaction is reversed by hydroxyl ions.[130]



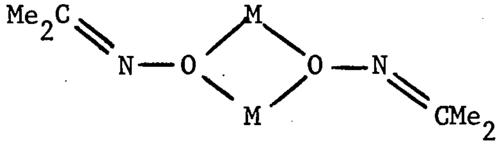
The trimethyl derivatives of aluminium gallium, indium and thallium, and methyl lithium all reacted at or below room temperature with acetoxime, with the cleavage of methane and the formation of the acetoxime derivatives, $Me_2MON=CMe_2$. They were all moisture sensitive compounds, and with the exception of the lithium compound, were sufficiently volatile to be sublimed under a good vacuum. Cleavage of methane by trimethylboron could only be accomplished at 95-100°C. The product, $Me_2BON=CMe_2$, was much more volatile than the other derivatives, and could readily be moved about on the vacuum line. It was found to be monomeric in the vapour phase, partly associated in solution, and may be dimeric in the crystal.[131] This behaviour contrasts that reported by Inatome and Kuhn[127] for their "BON-BON" compounds, which were dimeric in methyl cyanide solution. This difference is more likely to be due to the weaker donor strength of the nitrogen in acetoxime than the nitrogen in hydroxylamine, rather than to any steric effects.

The dimethyl-aluminium, gallium, and indium derivatives of acetoxime, were all found to be dimeric in benzene solution, and mass spectroscopy shows the aluminium to be dimeric in the vapour phase. The Structure I shown below is proposed for their mode of association,



I

rather than II

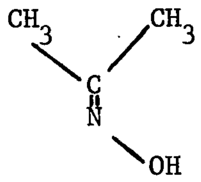


II

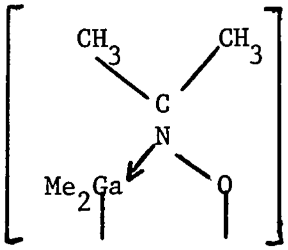
for reasons which will be described below.

Nuclear Magnetic Resonance Spectra

The nuclear magnetic resonance spectra of these compounds were recorded in carbon tetrachloride, benzene and deuterotoluene as solvents with tetramethyl-silane as internal reference. The results are listed in Table XVII, together with assignments for the peaks, and a typical spectrum is shown in Photograph III. Splitting of the peak assigned to the C-Me protons was observed in benzene and other aromatic solvents, and was found to be absent in all aliphatic solvents. This splitting may arise from the different environments of the carbon-methyl protons,



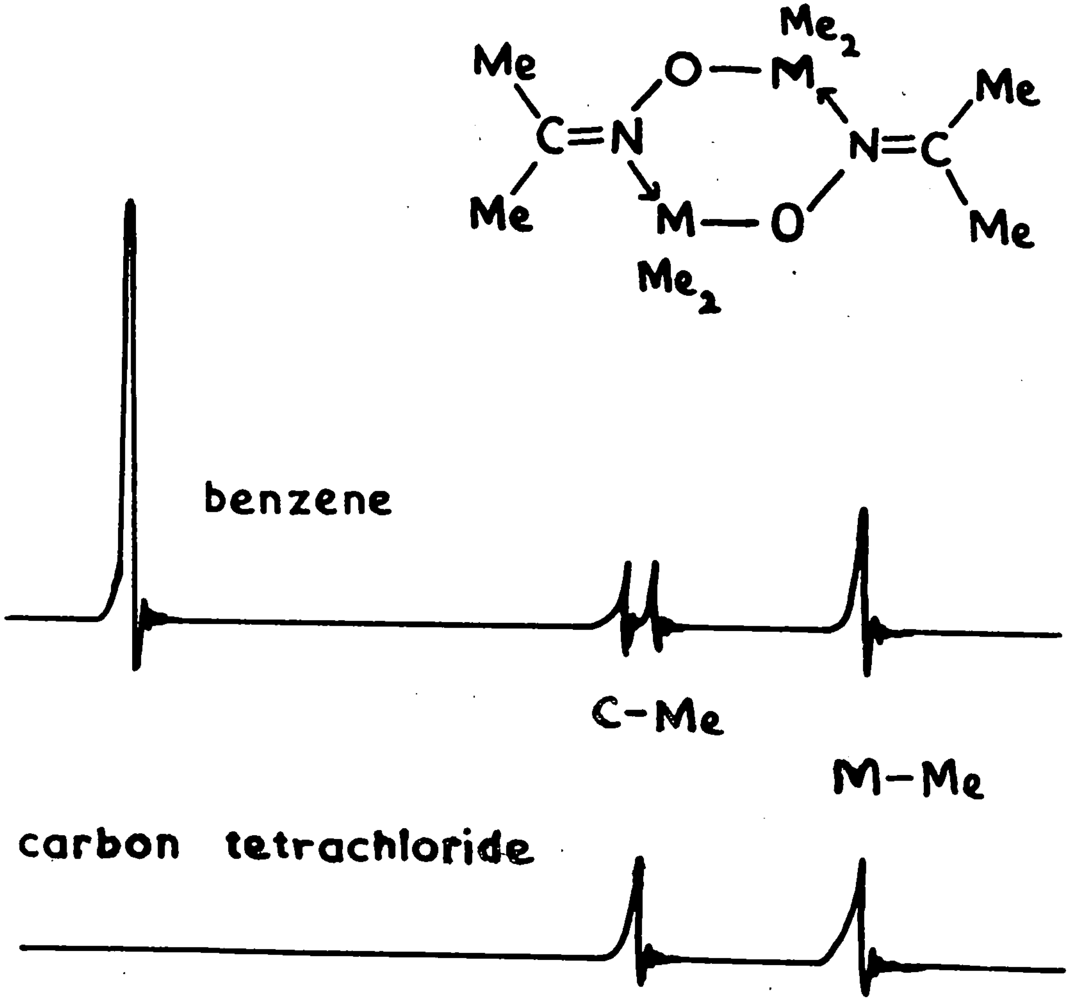
or



but it is not known why it should occur in an aromatic solvent and not in an aliphatic solvent. Splitting of the methyl peaks in acetoxime has

PHOTOGRAPH III.

N.M.R. SPECTRA



been reported,[132] and was suggested to arise from a 50% mixture of syn- and anti-forms, but this is clearly not the case.

No metal-proton coupling was observed, except in the case of the thallium compound, when the peak due to the protons of the Tl-Me group was found to be a doublet (τ= 9•00, J = 378 c.p.s.). Thallium-proton coupling has been previously observed. The proton magnetic resonance spectrum of trimethylthallium in methylene chloride solution at -85°C is a doublet with τ= 9•48 and J = 251 c.p.s.[133]

Infrared Spectra

The infrared spectra of all the acetoxime derivatives were recorded as nujol mulls, and the infrared spectra in the vapour phase of the boron and gallium compounds were recorded, using a heated gas cell.

The infrared spectra of the boron compound are shown in Photograph IV. The marked differences are caused by the change of association from the solid to the vapour phases. Detailed assignments are difficult to make because the similarity in masses of the atoms making up this compound causes much superimposition of absorption bands, especially in the vapour-phase spectrum. The bands at lower frequency in the spectrum of the nujol mull probably arise from skeletal vibrations of the "BON-BON" ring.

The infrared spectra of the aluminium, gallium and indium derivatives are all rather similar, the main differences being absorptions due to the methyl groups on the metal atoms. The spectrum of the gallium compound recorded as a nujol mull is very similar to the vapour phase spectrum

TABLE XVII

Proton Magnetic Resonance Spectroscopic Results.

Compound	Solvent	values of peaks (p.p.m.; $\tau_{Me_4Si} = 10{\cdot}00$)	
		C - Me	M - Me
$Me_2C{:}NOH$	CCl_4	8·14s	-
$(Me_2C{:}NOBMe_2)_n$	CCl_4	7·98s(1)	9·87(1)
$(Me_2C{:}NOGaMe_2)_2$	CCl_4	8·00s(1)	10·38s(1)
$(Me_2C{:}NOInMe_2)_2$	CCl_4	8·10s(1)	9·97s(1)
$Me_2C{:}NOH$	C_6H_6	8·22s(1), 8·33s(1)	-
$(Me_2C{:}NOBMe_2)_n$	C_6H_6	8·32s(1), 8·34s(1)	9·64s(2)
$(Me_2C{:}NOAlMe_2)_2$	$C_6D_5CD_3$	8·34s(1), 8·44s(1)	10·50s(2)
$(Me_2C{:}NOGaMe_2)_2$	C_6H_6	8·24s(1), 8·39s(1)	10·10s(2)
$(Me_2C{:}NOInMe_2)_2$	C_6H_6	8·22s(1), 8·35s(1)	10·16s(2)
$(Me_2C{:}NOTlMe_2)_n$	C_6H_6	8·20s(2)	9·00d(2) (J = 378 c.sec^{-1})

s = singlet; d = doublet; relative intensities in parentheses.

(Photograph V), and so the vapour and solid are considered to contain the same units of structure. Assignments where possible are shown in Table XVIII.

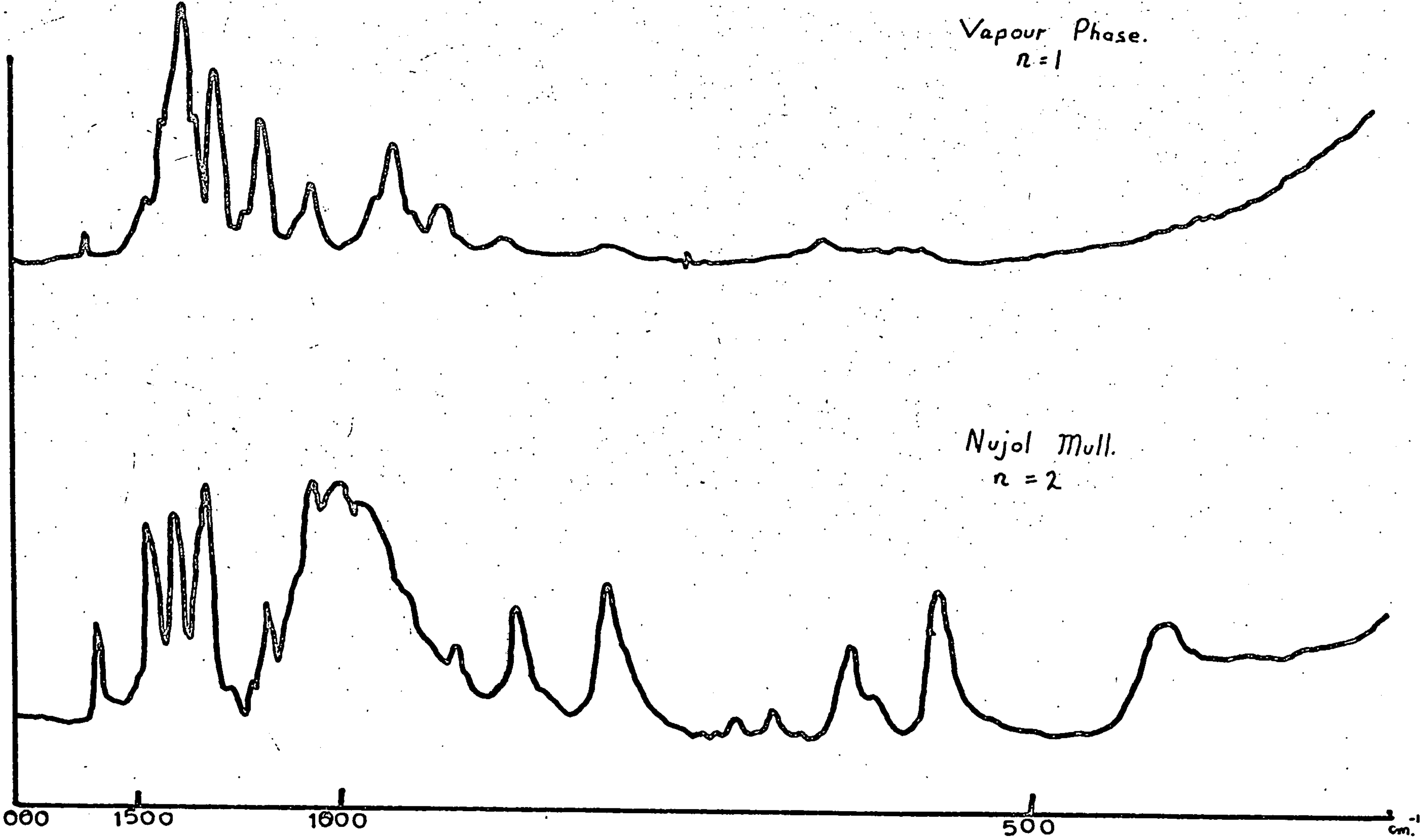
Table XVIII

	$(Me_2AlON:CMe_2)_2$	$(Me_2GaON:CMe_2)_2$	$(Me_2InON:CMe_2)_2$	$(Me_2TlON:CMe_2)_n$
$M\text{-}CH_3$ δsym.	1190	1200	1156	1170
$M\text{-}CH_3$ rock	735	735	704	791
$M\text{-}CH_3$ νantisym.	690	585	510	540
$M\text{-}CH_3$ νsym.	561	528	473	-
C-C ν	1282	1279	1261	1253
$C\text{-}CH_3$ rock	1092	1089	1076	1054

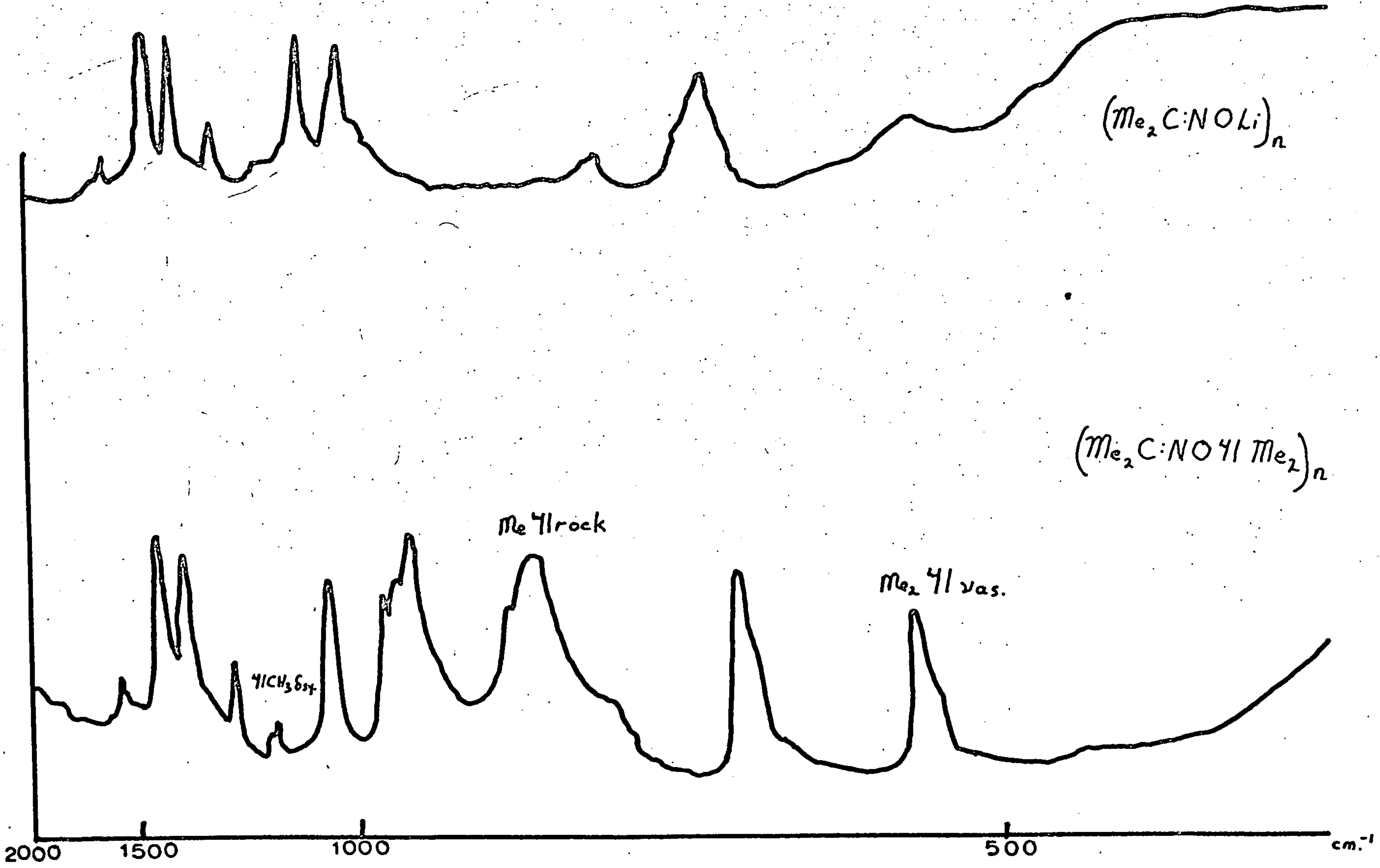
These assignments are based upon the assignments made for the dimethylamino-dimethyl(aluminium, gallium and indium) spectra,[95] the Raman spectra of dimethylthallium compounds,[134] e.g. $(Me_2Tl)^+ ClO_4^-$, and the infrared spectra of formaldoxime and acetoxime.[135]

The infrared spectra of the thallium and lithium derivatives (Photograph VI) are also very similar to each other, the only major differences arising from absorptions which may be assigned to the Me_2Tl part of the molecule. It is possible that these compounds have similar structures, especially in the acetoxime part of the molecule. Absorptions which can be assigned to $TlMe_2$ νsymm. are absent in the spectra recorded, Photograph IV

$(Me_2C{:}NOBMe_2)_n$



Photograph VI



and it is tempting to propose a linear $(Me\text{-}Tl\text{-}Me)^+$ skeleton, thus making the symmetrical stretching mode infrared inactive. The compound is readily crystallisable from ether and so such an "ionic"-type compound appears to be improbable.

Table XIX

Infrared Spectroscopic data for $(Me_2C{:}NOMMe_2)_n$

Compound	$\nu_{C=N}(cm^{-1})$	Compound	$\nu_{C=N}(cm^{-1})$
$Me_2C{:}NOH$	1678	$(Me_2C{:}NOGaMe_2)_2$	1630
$Me_2C{:}NOH^{*}$	1662	$(Me_2C{:}NOGaMe_2)_2^{*}$	1628
$(Me_2C{:}NOBMe_2)_2$	1649	$(Me_2C{:}NOInMe_2)_2$	1612
$Me_2C{:}NOBMe_2^{*}$	1663	$(Me_2C{:}NOTlMe_2)_n$	1595
$(Me_2C{:}NOAlMe_2)_2$	1635	$(Me_2C{:}NOLi)_n$	1610

* vapour phase; all others nujol mulls.

The absorptions arising from C=N stretching vibrations are listed in Table XIX. The frequency is highest for acetoxime, where the compound is monomeric in the gas phase, and hydrogen-bonded through the nitrogen in the crystal phase,[136] and for the vapour phase spectrum of dimethylboron acetoximate. The frequency is significantly lower in the nujol mull spectrum and in all the other metal derivatives. In complexes formed between compounds containing carbonyl groups and Lewis acids, $R_2C{=}O \longrightarrow MXn$, the carbonyl frequency is lowered[137] (contrary to cyanide coordination complexes) and this has often been used to determine whether coordination involves the carbonyl group in compounds containing other possible donor atoms, e.g. acid chlorides or ketones. By analogy with this, it seems likely that the lowering of the C=N stretching frequency in the boron compound, on passing from the monomeric gas to the polymeric crystal, arises from coordination of the nitrogen to the boron atom, and again by analogy it is likely that the other metal derivatives are also associated through the nitrogen. There is virtually no change in frequency in the gallium compound on passing from the crystal phase to the vapour phase implying that there is no change in the mode of association during this phase change.

Mass Spectra

The mass spectra of the boron and aluminium compounds were recorded, and showed them to be monomeric and dimeric respectively in the gas phase. Preliminary studies on the breakdown patterns show them to be consistent with previously formulated structures for these compounds.

A molecular ion is observed for the monomer of the boron compound and the most intense peaks in the spectrum correspond to the fragments formed by fission of the nitrogen-oxygen bond.

$$Me_2BON{=}CMe_2 \longrightarrow [Me_2B \overset{\cdots}{-\!-} O]^+ \quad \text{and} \quad [Me_2C{=}N]^+$$

No molecular ion is observed for the dimer of the aluminium compound, but fragments formed by loss of one, two and three methyl groups from the dimer are observed. No intense peak is observed at mass 56, due to $[Me_2C{=}N]^+$ and this is powerful evidence in favour of Structure I rather than Structure II (see page 118) where fission of the nitrogen-oxygen bond would be expected to be the first stage in the breakdown.

The final evidence in favour of the dimer being associated through the nitrogen is furnished by the crystal structure of acetoxime itself.[136] The acetoxime molecules form sheets of planar trimers which are held together by N ----- H-O bonds. The fact that the crystal is held together by hydrogen bonding through the nitrogen rather than the oxygen implies that the former is more basic in character than the latter, and this naturally becomes the mode of association in the metal oxime derivatives.

APPENDIX

For a peak at a given mass in the mass spectrum of a compound, there can be several numerical combinations of the atoms to give that integral mass, e.g. mass 14 = $^{11}BH_3$, CH_2 or N. When the mass number becomes higher, the number of atom combinations becomes progressively larger, and eventually it becomes an extremely laborious task to work out manually all the combinations possible. This was the case during the mass spectroscopic investigation into Fraction III from the reaction of methyl cyanide with diborane (see page 34 in the experimental section). When this became apparent, a program in Algol, for use on an Elliot 803 computer, was written. Two variations were developed and are discussed below.

Variation I

The first variation is shown below as Program I.

This variation lists out all the possible carbon, hydrogen boron (^{11}B only) and nitrogen combinations for any integral mass, and prints out all these combinations together with the accurate mass. The maximum number of hydrogen atoms allowed has been limited to the number of unoccupied valencies on each of the atoms of the fragment, i.e. the number of hydrogen atoms cannot be greater than [(2 x the number of carbon atoms) + 2 + (2 x the number of boron atoms) + (the number of nitrogen atoms)]. The only compound which this limitation omits is the diborane-ammonia adduct which undergoes immediate thermal decomposition under the conditions in which a mass spectrum is recorded. The maximum number of boron and nitrogen

PROGRAM I

```
RJ ATOM COMB 1,4'

BEGIN INTEGER C,H,B,N,INMASS, BL, NL,1'
REAL MH,MB,MN,MASS'
SWITCH S:=REPEAT,FINISH,NEXTMASS,REENTRY'

READ BL,NL,1'
MH:=1·007825' MB:=11.009307' MN:=14.003074'

PRINT ££L? RJ ATOM COMB 1,4.£L6??'

NEXTMASS: READ INMASS'

PRINT ££L6?CARBON,HYDROGEN,BORON AND NITROGEN COMBINATIONS.?'
PRINT ££L4?MASS =?,SAMELINE,DIGITS(3),INMASS,
££L2?  C  H  B  N    MASS£L??'

FOR B:=0 STEP 1 UNTIL BL DO
    BEGIN FOR N:=0 STEP 1 UNTIL NL DO
       BEGIN C:=(INMASS-B×11-N×14) DIV 12'
             H:=INMASS-B×11-N×14-C×12'
            IF C=0 AND N=0 AND H LESSEQ B×3 THEN GOTO REENTRY'
            IF C=0 AND B=0 AND H LESSQ N×3 THEN  GOTO REENTRY'
       REPEAT:  IF C LESS 0 OR H LESS 0 OR H GR (2×C
                +2+N+2×B) THEN GOTO FINISH'
    REENTRY:IF H LESS O THEN GOTO FINISH'
            MASS:=C×12.0000+H×MH+B×MB+N×MN'
              PRINT DIGITS(2),C,SAMELINE,H,B,N,£  ?,ALIGNED(1,5),
              (MASS-ENTIER(MASS))'
            C:=C-1'     H:=H+12'
           GO TO REPEAT'
       FINISH:'      END'
         END'
1:=1-1'
IF 1 GR 0 THEN GOTO NEXTMASS'
END OF PROGRAM.'
```

atoms is also limited, but this limitation may be altered at will, and is punched out each time on the data tape. The data tape takes the following form:-

Limiting number of boron atoms.

Limiting number of nitrogen atoms.

The number of masses to be evaluated.

The integral masses to be evaluated.

The information is given in the following form:-

```
CARBON, HYDROGEN, BORON AND NITROGEN COMBINATIONS.

MASS = 68

 C    H    B    N     MASS

 5    8    0    0   0.06260
 4    6    0    1   0.05002
 3    4    0    2   0.03745
 2    2    0    3   0.02487
 1    0    0    4   0.01230
 4    9    1    0   0.07973
 3    7    1    1   0.06716
 2    5    1    2   0.05458
 1    3    1    3   0.04200
 0    1    1    4   0.02943
 3   10    2    0   0.09686
 2    8    2    1   0.08429
 1    6    2    2   0.07171
 0    4    2    3   0.05914
 2   11    3    0   0.11400
 1    9    3    1   0.10142
 0    7    3    2   0.08884
 2    0    4    0   0.03723
 1   12    4    0   0.13113
 0   10    4    1   0.11855
```

PROGRAM II

```
RJ ATOM COMB 1,5.'

BEGIN INTEGER C,H,B,N,INMASS,BL,NL,I,X'
REAL MH,MB,MASS,EXPMASS,RESOLUTION'
SWITCH SS:=REPEAT,FINISH,NEXT1MASS,NEXT2MASS,REENTRY,LABEL1'

READ BL,NL,1,X'
MH:=1,007825' MB:=11.009307' MN:=14.003074'

PRINT ££L? RJ ATOM COMB 1,5.£L6??'

NEXT1MASS:  READ RESOLUTION'
NEXT2MASS:  READ EXPMASS'

PRINT ££L6?CARBON,HYDROGEN,BORON AND NITROGEN COMBINATIONS.?'

INMASS:=IF (EXPMASS-ENTIER(EXPMASS))  GREQ 0.5 THEN
          ENTIER(EXPMASS)+1 ELSE ENTIER (EXPMASS)'

PRINT ££L4?MASS =?,SAMELINE,DIGITS(3),INMASS,
SAMELINE,£EXPERIMENTAL MASS=?,SAMELINE,ALIGNED(3,5),EXPMASS,
££L2?  C   H   B   N      MASS£L??'

FOR B:=0 STEP 1 UNTIL BL DO
    BEGIN FOR N:=0 STEP 1 UNTIL NL DO
       BEGIN C:=(INMASS-B×11-N×14) DIV 12'
             H:=INMASS-B×11-N×14-C×12'
            IF C=0 AND N=0 AND H LESSEQ B×3 THEN GOTO REENTRY'
            IF C=0 AND B=0 AND H LESSEQ N×3 THEN GOTO REENTRY'
      REPEAT:  IF C LESS 0 OR H LESS 0 OR H GR (2×C
                 +2+N+2×B) THEN GOTO FINISH'
    REENTRY:IF H LESS 0 THEN GOTO FINISH'
            MASS:=C×12.0000+H×MH+B×MB+N×MN'
         IF ABS (MASS-EXPMASS) GR (RESOLUTION×EXPMASS)
                       THEN GOTO LABEL1'

          PRINT DIGITS(2),C,SAMELINE,H,B,N,£  ?,ALIGNED(1,5),
              (MASS-ENTIER(MASS))'
      LABEL1: C:=C-1'  H:=H+12'
                GOTO REPEAT
     FINISH:'       END'
        END'
1:=1-1'
IF 1 GR 0 THEN GOTO SS(X)'
END OF PROGRAM'
```

Variation II

The second variation is shown below as Program II.

This program calculates all the possible atom combinations, and the accurate masses of all these combinations, but prints out only those which are within a predetermined range of the measured mass, and this range is most conveniently chosen to be the resolution of the mass spectrograph under the operating conditions. The limitations on the number of hydrogen, boron and nitrogen atoms are the same as before. The data tape takes the following form:-

Limiting number of boron atoms.

Limiting number of nitrogen atoms.

The number of masses to be evaluated.

Either number 3 or number 4 depending upon whether the resolution of the instrument has been changed or not. If the resolution has not been changed read number 4.

The resolution.

The accurate masses of the peaks to be identified. If the resolution is not changed, the masses may be listed, otherwise the resolution for each peak must be given before the accurate mass.

The information is given in the following form, shown on the next page.

CARBON,HYDROGEN,BORON AND NITROGEN COMBINATIONS.

MASS = 109
EXPERIMENTAL MASS = 109.11500

C	H	B	N	MASS
7	14	1	0	0.11886
4	11	2	2	0.11084
2	10	3	3	0.11539
0	9	4	4	0.11995

CARBON, HYDROGEN;BORON AND NITROGEN COMBINATIONS.

MASS = 108
EXPERIMENTAL MASS = 108,11410

C	H	B	N	MASS
7	13	1	0	0.11103
5	12	2	1	0.11559
0	8	4	4	0.11212

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