Reactions of niteiles with some organic compounds of boron and aluminium

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REACTIONS OF NITRILES
WITH SOME ORGANIC COMPOUNDS
OF
BORON AND ALUMINIUM

by

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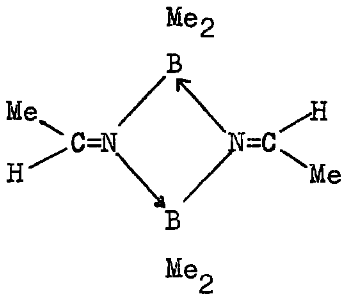
MEMORANDUM

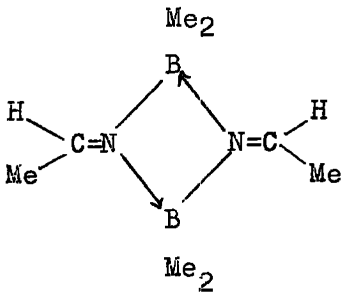
The work included in this thesis was carried out at the Science Laboratories of the University of Durham between September 1961 and July 1964, and has not been submitted for any other Degree. Part of this work has already been the subject of a publication in the Journal of the Chemical Society. All the work described is the original work of the author, except that acknowledged by reference.

Summary

Dimeric ethylideneaminodialkylboranes, $(MeCH{:}N.BR_2)_2$ (R = Me or Et) have been prepared from methyl cyanide and the appropriate tetra-alkyldiborane, R_2BHBHR_2, in the latter case N-triethylborazine being formed also. Isomeric forms of the methyl compound, $(MeCH{:}N.BMe_2)_2$, have been separated, one a crystalline solid, m.p. 76°, v.p. 0.6 mm. at 20°, the other a liquid, f.p. *ca.* -5°, v.p. 1.8 mm. at 20°. Their infrared and H' nuclear magnetic resonance spectra indicate that the solid isomer has the *trans* structure I and that the liquid has the *cis* structure II.



I



II

Such structures are supported by the detection of dimethylborinic acid, acetaldehyde and ammonia, but not ethylamine, among their hydrolysis products, and the formation of dimethylchloroborane by reaction with hydrogen chloride.

Aluminium compounds with related structures have been isolated from reactions between nitriles and organoaluminium compounds, that

is, adducts RCN,AlR'_3 rearrange by transfer of organic groups R' from the aluminium to the carbon atom of the cyanide group:

$$RCN + AlR'_3 \longrightarrow RCN,AlR'_3 \longrightarrow (RR'C{:}N.AlR'_2)_2$$

Thus, adducts of phenyl cyanide with trimethyl- and triphenylaluminium rearrange at temperatures between 150° and 250° to form substituted benzylideneaminoaluminium compounds, $(R'PhC{:}N.AlR'_2)_n$.

The adduct of triethylaluminium and phenyl cyanide, $PhCN,AlEt_3$ loses ethylene when heated and subsequent transfer of hydrogen leads to $(PhCH{:}NAlEt_2)_2$.

Adducts of methyl or ethyl cyanide with organoaluminium compounds rearrange when heated to form dimers $(MeR'C{:}N.AlR'_2)_2$ and $(EtR'C{:}NAlR'_2)_2$ although these are obtained in low yield (20%) because at similar temperatures the adducts evolve hydrocarbon R'H through loss of one of the acidic hydrogen atoms of the nitrile, leaving polymeric solids of the type $(\rightarrow AlMe_2.CH_2CN\rightarrow)_n$ and $(-AlMe.CH_2CMe{:}N-)_m$.

Dimethylaluminium chloride reacts in a similar manner to trimethylaluminium. Dimethylaluminium hydride reacts with these nitriles by immediate transfer of hydrogen at room temperature to form $(RCH{:}N.AlMe_2)_n$.

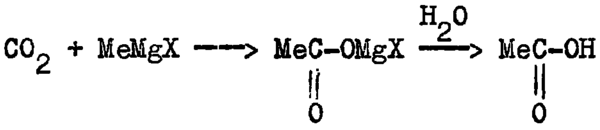
These reactions establish the nature of the intermediates which were involved in reactions reported by other workers who have shown that nitriles can be converted into ketones, aldehydes or amines by reaction with suitable organo-aluminium compounds.

Introduction

The reactions which have been investigated in this work are examples of a type of addition reaction in which a group consisting of a relatively electropositive element, M, bound to a comparatively electronegative element X, adds across a multiple bond A=B.

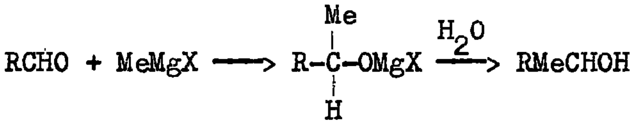
i.e. $\text{M-X} + \text{A=B} \longrightarrow \text{M-A-B-X}$

The generality of this reaction has recently been commented on by Bloodworth and Davies.[1] Reactions of this type have proved particularly useful in syntheses. Among well-known examples are the reactions between Grignard (or lithium) reagents[2] and compounds containing C=O or C≡N groups; e.g. the carbonation of Grignard reagents by carbon dioxide,

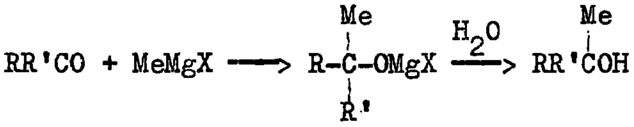


$$CO_2 + \text{MeMgX} \longrightarrow \text{Me}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-OMgX} \xrightarrow{H_2O} \text{Me}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-OH}$$

the formation of alcohols from aldehydes and ketones,

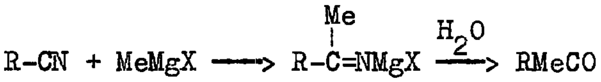


$$\text{RCHO} + \text{MeMgX} \longrightarrow \text{R-}\overset{\overset{\text{Me}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}\text{-OMgX} \xrightarrow{H_2O} \text{RMeCHOH}$$



$$\text{RR'CO} + \text{MeMgX} \longrightarrow \text{R-}\overset{\overset{\text{Me}}{|}}{\underset{\underset{\text{R'}}{|}}{\text{C}}}\text{-OMgX} \xrightarrow{H_2O} \text{RR'}\overset{\overset{\text{Me}}{|}}{\text{C}}\text{OH}$$

and the formation of ketones from nitriles,



$$\text{R-CN} + \text{MeMgX} \longrightarrow \text{R-}\overset{\overset{\text{Me}}{|}}{\text{C}}\text{=NMgX} \xrightarrow{H_2O} \text{RMeCO}$$

A more recently discovered example is the hydroboration of olefinic and acetylenic compounds,[3]

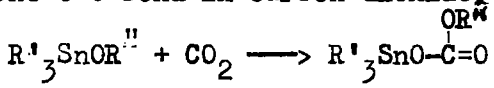
$$R\text{-}CH{=}CH_2 + R'_2BH \longrightarrow RCH_2CH_2BR'_2$$

affording a route from olefins to, for example, alcohols, if the resulting organoborane is oxidised by peroxide.

The reaction of aluminium alkyls with olefins[4] has been used to prepare paraffin polymers and various 1-alkenes; the growth step in this reaction involves addition of R-Al across C=C bonds,

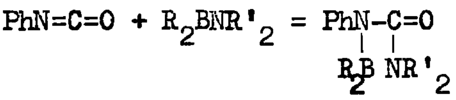
$$RAl/_3 + nC_2H_4 \longrightarrow R(C_2H_4)_nAl/_3 \xrightarrow{200^\circ C} R_2(C_2H_4)_{n-1}CH{=}CH_2 + HAl/_3$$

The examples already quoted involve organo-or hydrido- derivatives; other derivatives show similar reactions to a more limited extent. Thus, it has been shown that the tin-oxygen[1] group of tin alkoxides will add across the C=O bond in carbon dioxide.



$$R'_3SnOR'' + CO_2 \longrightarrow R'_3SnO\text{-}\overset{\displaystyle OR''}{\overset{|}{C}}{=}O$$

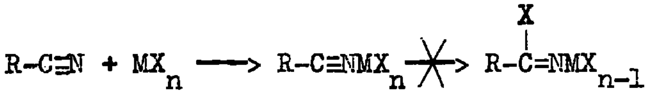
and the boron-nitrogen group of an aminoborane will add across the N=C bond in phenyl isocyanate,[5]



$$PhN{=}C{=}O + R_2BNR'_2 = \underset{\displaystyle R_2B}{\underset{|}{PhN}}\text{-}\underset{\displaystyle NR'_2}{\underset{|}{C}}{=}O$$

In the present work an investigation has been made of the reactions between <u>nitriles</u> and <u>organo</u>- and <u>hydrido</u>- compounds of <u>boron</u> and <u>aluminium</u>.

Nitriles, RCN, are known to react with a variety of Lewis acids, MX_n, to form 1:1 adducts $RCN{\rightarrow}MX_n$. Studies[6] on the infrared spectra of such adducts have shown the position of the C≡N absorption band to vary with the Lewis acid, MX_n, being shifted to a higher frequency than that of the corresponding band in the free nitrile. When the Lewis acid is a metal halide these adducts do not normally rearrange to give a compound containing C=N.



$$R{-}C{\equiv}N + MX_n \longrightarrow R{-}C{\equiv}NMX_n \not\longrightarrow R{-}\overset{\overset{X}{|}}{C}{=}NMX_{n-1}$$

In those cases where the rearrangement does take place, as for example when MX_n is a Grignard reagent, the rearranged material is usually not isolated but hydrolysed to give a ketone.

In the following pages a review is made of reactions in which compounds of boron or aluminium are known to add to multiply bonded systems; a short section follows in which addition reactions of nitriles are summarised.

Reactions of Boron compounds with unsaturated compounds

Hydroboration

Stock, in 1923, recorded that an unsaturated hydrocarbon would react with diborane, and above 100°C acetylene would react explosively.[7] Until 1948, when Hurd[8] reported that diborane would react with olefines to form trialkylboranes and with benzene to form phenyl boron compounds, no further experiments were reported. The reactions were done using only small amounts of diborane with relatively large amounts of hydrocarbon at temperatures above 100°C in sealed glass tubes, and only small amounts of products were produced.

$$6RCH{=}CH_2 + B_2H_6 \longrightarrow 2(RCH_2CH_2)_3B$$

Stone and Emeléus reported two years later that diborane would act as a Lewis acid catalyst of certain polymerisation reactions similarly to boron trifluoride.[9] Thus, at low temperatures diborane converted ethylene and propylene oxides into oligomers of four or six units per molecule. The reaction was extremely slow with acrylonitrile, methyl methacrylate and especially styrene which reacted as previously reported by Hurd.

In 1956 a discovery was made which allowed the hydroboration reaction to assume importance in syntheses, when it was observed by H.C. Brown and his co-workers that ethers and other similar weak bases, used as solvents, greatly catalysed the addition of boron-hydrogen groups across multiple bonds so that the reaction could be carried out under mild conditions,[10] contrary to what had been indicated from earlier work.[8] The most convenient preparation of diborane was from sodium borohydride and boron trifluoride-ether complex:[11]

$$3NaBH_4 + 4BF_3.OEt_2 \longrightarrow 2B_2H_6 + 3NaBF_4 + 4Et_2O$$

This reaction is conveniently carried out in an ether solvent, commonly diglyme (diethyleneglycol dimethyl ether), and the diborane produced is allowed to react in situ with an olefin;

$$12RCH{=}CH_2 + 3NaBH_4 + 4BF_3OEt_2 \longrightarrow 4(RCH_2CH_2)_3B + 3NaBF_4 + 4Et_2O$$

Diglyme is most often used because both diborane and sodium borohydride are readily soluble in it, and because it is miscible with water, allowing easy separation of the products.

Alternatively the diborane may be bubbled, in a stream of nitrogen, through a solution of the olefin dissolved in an appropriate ether. Tri-n-hexylborane, for example, may be obtained in a 90% yield by bubbling diborane through a solution of 1-hexene in tetrahydrofuran:[12]

$$6Bu^nCH{=}CH_2 + B_2H_6 \longrightarrow 2(C_6H_{13})_3B$$

Although these two methods are most generally advocated, variations on them are possible. The essential ingredients are a hydride, which need not contain boron (e.g. $LiBH_4$, $NaBH_4$, KBH_4, $LiAlH_4$, LiH, NaH, $C_5H_5N.BH_3$, or $Me_3N.BH_3$), an acid, which must contain boron if the hydride does not, (e.g. BF_3, BCl_3, $AlCl_3$, $AlCl_3 + B(OMe)_3$, HCl or H_2SO_4), and a suitable weak base as solvent, most often an ether, having a boiling point which allows easy separation of the products. Amineboranes, R_3N,BH_3, are less convenient as sources of boron hydride than metal hydrides for the hydroboration of olefins because they require higher temperatures (100-200°C).

The uses to which hydroboration can be put depend on the reactions shown by organoboranes. The most generally useful are as follows:

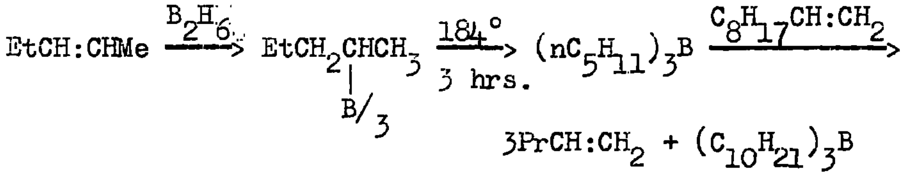
1. alkaline hydrogen peroxide gives an alcohol,

$$R_3B + 3H_2O_2 + NaOH \longrightarrow 3ROH + NaB(OH)_4$$

2. protonation with acetic acid gives a hydrocarbon,[13]

$$R{-}B\langle + HOAc \longrightarrow RH + \rangle BOAc$$

3. heating, followed by treatment with an involatile olefin yields an isomer of the parent olefin, (i.e. contra-thermodynamic isomerisation)[14]



$$EtCH{:}CHMe \xrightarrow{B_2H_6} \underset{\substack{|\\ B/_3}}{EtCH_2CHCH_3} \xrightarrow[3\ hrs.]{184^\circ} (nC_5H_{11})_3B \xrightarrow{C_8H_{17}CH{:}CH_2} 3PrCH{:}CH_2 + (C_{10}H_{21})_3B$$

4. oxidation with chromic acid to give ketones or acids,[15]

5. treatment with alkaline silver nitrate causes coupling of the alkyl groups, probably by transfer of alkyl groups from the boron to the silver followed by decomposition of the silver alkyl.[16]

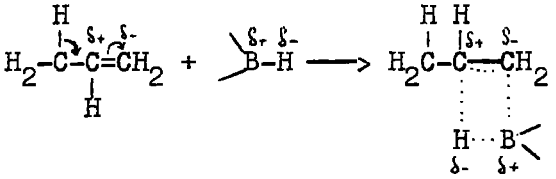
The direction of addition of B-H bonds to olefins is highly specific, the boron atom becoming most often attached to the less substituted carbon atom of the double bond.[17] For example, treatment of a mixture of 1- and 2-pentene with a deficiency of diborane results in the selective conversion of the terminal olefin into tri-n-pentylborane,[18]

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

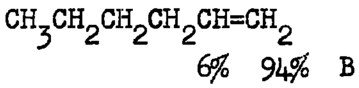
This direction of addition can be determined by treatment of the organoborane with alkaline hydrogen peroxide which gives the corresponding alcohol,

$$(\text{RCH}_2\text{CH}_2)_3\text{B} \xrightarrow[\text{OH}^-]{\text{H}_2\text{O}_2} 3\text{RCH}_2\text{CH}_2\text{OH} + \text{B(OH)}_3$$

when the hydroxyl group becomes attached to the carbon atom formerly bound to the boron. The stereospecific nature of the B-H addition is explained by the polarity of the B-H group and of the olefin. If the B-H group has a slight separation of charge thus $>\overset{\delta+}{\text{B}}-\overset{\delta-}{\text{H}}$ and the unsymmetrical olefin a polarity thus ${}^{\text{R}}_{\text{H}}\!>\!\overset{\delta+}{\text{C}}{:}\overset{\delta-}{\text{CH}_2}$ then addition will be directed as follows:

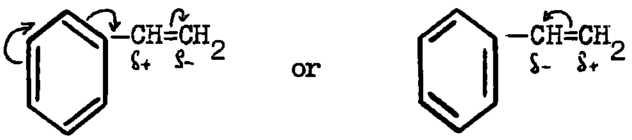


1-Hexene gives with diborane 94% of the boron attached to the terminal position and 6% on the adjacent carbon atom:[17]

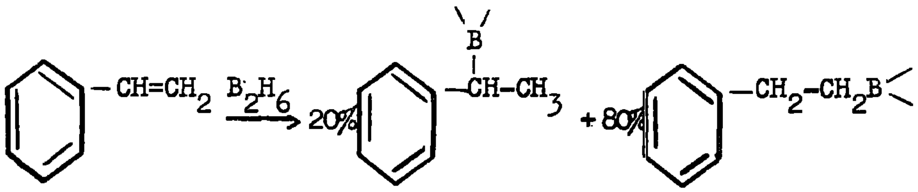


$$\underset{\qquad\qquad\qquad\qquad 6\% \quad 94\% \quad B}{\mathrm{CH_3CH_2CH_2CH_2CH{=}CH_2}}$$

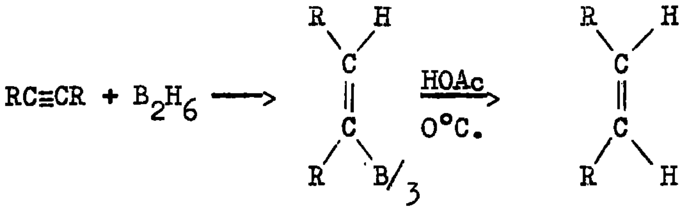
Aryl olefins tend to give larger yields of the minor product because they are more readily polarised in either direction:



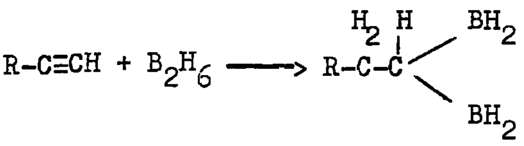
Styrene with diborane gives 20% of the boron attached to the α-carbon atom and 80% on the β-carbon atom:[17]



Diborane also reacts with <u>acetylenic</u> triple bonds.[19] Non-terminal C≡C groups react to give vinyl boranes which can be hydrolysed to <u>cis</u>-olefins



Terminal acetylenes are completely reduced by the addition of two B-H bonds,



unless the hydroborating agent is an organoborane $(R_2BH)_2$ in which the alkyl groups, R, are bulky. Di-sec-isoamylborane (also called disiamylborane) is a useful reagent of this type and can itself be prepared from the hydroboration of 2-methyl-2-butene.[20,21]

$$B_2H_6 + \text{excess } Me_2C{=}CHMe \xrightarrow{\text{fast}} [(Me_2CHCHMe)_2BH]_2 \xrightarrow{\text{very slow}} (Me_2CHCHMe)_3B$$

The bulky alkyl groups on this compound prevent reaction with sterically hindered olefins and allow the boron to become attached almost exclusively to the more accessible carbon atom:

$$1 \text{ hexene} + R_2BH \longrightarrow CH_3CH_2CH_2CH_2\underset{1\%B}{CH}{=}\underset{99\%\ B}{CH_2}$$

Its use in the hydroboration of styrene leads to only two per cent of the α-derivative.

Reaction of diborane with other functional groups, e.g. C=O or C=N etc.

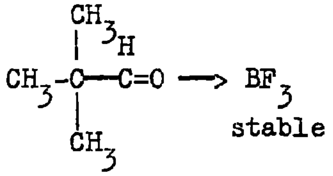
Diborane does not react with most functional groups of the type C=X or C≡X as easily as it does with carbon-carbon double and triple bonds, unless the groups contain reactive hydrogen as, for example, carboxylic acids.[22,23,24,25] This allows selective reduction of particular groups in the molecule to take place without the other groups being affected. Reactivities towards diborane decrease in the following order: carboxylic acids > olefins > ketones > nitriles > epoxides > esters. In tetrahydrofuran aldehydes and ketones react rapidly to give dialkoxyboranes:

$$2\,\mathrm{RCHO} + {}^{1}/2\mathrm{B_2H_6} \longrightarrow \mathrm{(RCH_2O)_2BH} \xrightarrow{3\mathrm{H_2O}} 2\mathrm{RCH_2OH} + \mathrm{B(OH)_3} + \mathrm{H_2}$$

Nitriles and carboxylic acids are also reduced but esters react much more slowly and acid chlorides not at all. The intermediate compounds are not usually isolated but hydrolysed to give the required product.[25]

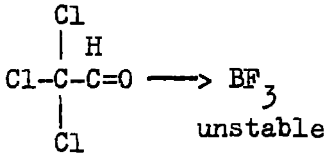
$$\mathrm{R-C{\equiv}N} + [\mathrm{BH_3}] \xrightarrow{3\mathrm{H_2O}} \mathrm{R-CH_2NH_2} + \mathrm{B(OH)_3} + \mathrm{H_2}$$

These reactions probably proceed via borane adducts, e.g. $\mathrm{R_2CO{\rightarrow}BH_3}$ or $\mathrm{RCN{\rightarrow}BH_3}$. It is significant that the aldehydes and ketones which react with diborane also form stable addition compounds with boron trifluoride. For instance, 2-dimethylpropionaldehyde forms a stable addition compound with boron trifluoride whereas chloral does not:



$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{C}=O \longrightarrow BF_3}$$

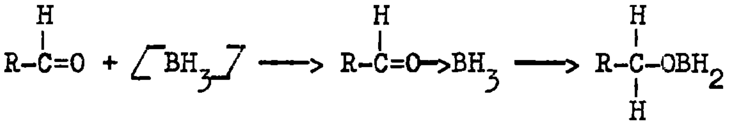
stable



$$\mathrm{Cl-\overset{Cl}{\underset{Cl}{C}}-\overset{H}{C}=O \longrightarrow BF_3}$$

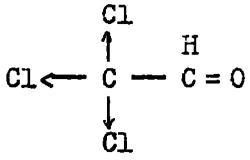
unstable

Diborane reduces $\mathrm{Bu^tCHO}$ but not $\mathrm{CCl_3CHO}$ under mild conditions.[22] It was therefore suggested that the overall reaction between aldehydes and diborane proceeded thus:



$$\mathrm{R-\overset{H}{C}=O} + [\mathrm{BH_3}] \longrightarrow \mathrm{R-\overset{H}{C}=O{\rightarrow}BH_3} \longrightarrow \mathrm{R-\overset{H}{\underset{H}{C}}-OBH_2}$$

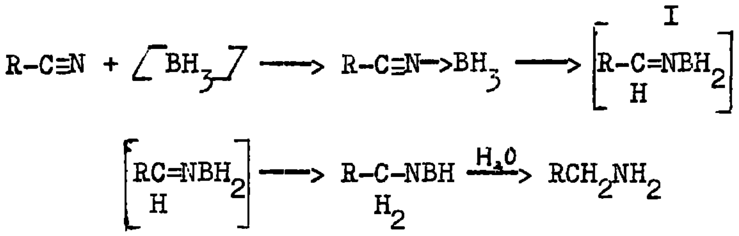
The chlorine in chloral would tend to withdraw electrons from the C=O group reducing its ability to donate electrons to the boron.



$$Cl \leftarrow \overset{\overset{Cl}{\uparrow}}{\underset{\underset{Cl}{\downarrow}}{C}} - \overset{H}{C} = O$$

This mechanism can be extended to the nitriles. The donor properties of the nitrogen atom enable a stable boron trifluoride addition compound, $RCN \rightarrow BF_3$, to be formed and similarly diborane attacks the group rapidly via a related borane adduct $RCN \rightarrow BH_3$. Some such adducts have in fact been isolated and characterised as thermally unstable solids.

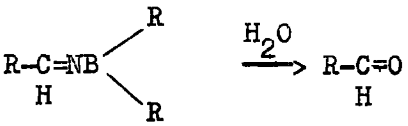
In tetrahydrofuran diborane reacts rapidly with nitriles to give products which may be hydrolysed to the corresponding amines:



$$R-C\equiv N + [BH_3] \longrightarrow R-C\equiv N \rightarrow BH_3 \longrightarrow \overset{I}{\left[\underset{H}{R-C}=NBH\right]_2}$$

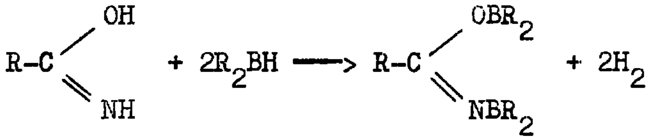
$$\left[\underset{H}{RC}=NBH\right]_2 \longrightarrow \underset{H_2}{R-C}-NBH \xrightarrow{H_2O} RCH_2NH_2$$

On the other hand a reagent with two alkyl groups of the type, $(R_2BH)_2$, such as disiamylborane[26] stops at the first stage (I) and on hydrolysis yields an aldehyde:



$$\underset{H}{R-C}=NB\begin{matrix}\diagup R\\ \diagdown R\end{matrix} \xrightarrow{H_2O} \underset{H}{R-C}=O$$

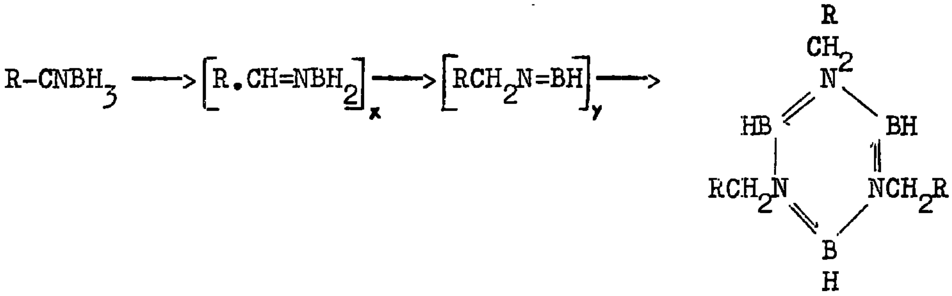
None of the intermediates was isolated. Disiamylborane used as a 1.0 molar solution in tetrahydrofuran reacted at 0°C only slowly with nitrile and nitro-groups since after 75 hours the reaction was not complete, but it reduced aldehydes and ketones easily to the corresponding alcohols. Primary acid amides liberated two moles of hydrogen but were not reduced:



The results show that diborane will reduce more groups than dialkylboranes but that the selectivity of the latter makes them useful reagents in certain cases where reaction with particular functional groups is necessary.

Apart from these studies of relative reactivities of various functional groups towards boranes the reactions with cyanides have been investigated in some detail, and in two cases intermediates of the form $(\mathrm{R{-}\underset{H}{C}{=}NBRH})_2$ and $(\mathrm{R{-}\underset{H}{C}{=}NBH_2})_2$ have been isolated.

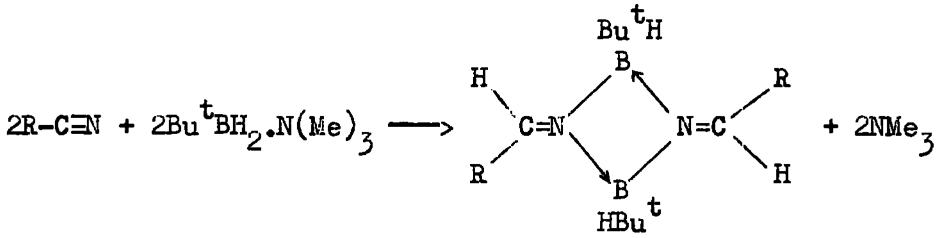
In 1942 Schlesinger and Burg[27] reported that a solid adduct could be formed from diborane and methyl cyanide $\mathrm{MeCN,BH_3}$. At room temperature it dissociated with slight decomposition and left, as well as unchanged gaseous reactants, an involatile liquid which was not identified. Burg[28] suggested that two hydrogen atoms had moved from the boron to the carbon atom of the cyanide group forming an N-substituted borazine, but he gave no evidence for this.



Further work[29] has shown this to be correct. The reactions of several cyanides with diborane showed that hydrogen atoms on the boron did move to the carbon of the cyanide group. The formation of the adduct MeCN,BH$_3$ was confirmed and from measurements of its dissociation pressure ($-34^\circ \rightarrow 4^\circ$C) gave 11.2 K.cals. as the heat of dissociation of the solid complex into methyl cyanide and diborane, <u>cf</u>, trimethylamine-borane Me$_3$NBH$_3$ 31.3 K cals/mole. The infrared spectrum of MeCN,BH$_3$ showed a band at 2280 cm.$^{-1}$ attributable to the $C\equiv N$ stretching mode but the ν(B-N) band was not identified.

This solid adduct decomposed at 20°C in a few days giving a colourless liquid which contained 50% of N'N"N"'triethylborazine. A minor product of the reaction was isolated in trace quantities and had a strong new band at 1685 cm.$^{-1}$ It was suggested that this band was the C=N stretching frequency and that the fraction isolated contained the intermediate $(CH_3CH{=}NBH_2)_n$ postulated in the mechanism of the reaction by Burg.[28] No further work was done on this compound.

However, during the course of the present investigation, some compounds have been reported[31] which have the formulae $(RCH{=}NBHBu^{t})_2$. These have been prepared from the reaction of trimethylamino-t-butylborane, $Me_3N.BBu^{t}H_2$, with various alkyl and aryl cyanides. Acetonitrile, propionitrile, n-butyronitrile and i-butyronitrile all reacted smoothly at 100°C in diglyme liberating trimethylamine. Molecular weight measurements and analyses indicated that the products were dimeric 1:1 adducts of t-butylborane and the corresponding nitrile. The infrared spectrum of each product contained a B-H stretching band at 2390 $cm.^{-1}$ and a C=N stretching band at 1660 $cm.^{-1}$ ^{11}B magnetic resonance spectra were interpreted as showing that the products were dimers of alkylideneamino-t-butyl boranes.



Several aryl derivatives were also prepared. Most of these, however, gave two pure crystalline fractions, one melting at about 140°C and the other at about 190°C. Heating the lower melting products above their melting points converted them into materials which melted nearer the higher melting point. In all cases a C=N stretching band was observed about 1640 $cm.^{-1}$

Hydrolysis of the products gave the corresponding aldehyde together with hydrogen and t-butylboronic acid:

$$(Bu^{t}BHN{=}CHPh)_2 \xrightarrow{H_2O} 2PhCHO + 2H_2 + NH_3 + 2Bu^{t}B(OH)_2$$

Molecular weight studies on the lower melting aryl derivatives showed them to be dimeric, $(RCH{=}NBHBu^{t})_2$ like the alkyl compounds. The higher melting isomers were too insoluble for molecular weight determinations to be carried out but were thought to be more highly polymeric, possibly trimers based on a six membered $(B{-}N)_3$ ring. In all these compounds the relative arrangement of the groups attached to boron and the carbon of the azomethine group can lead to several isomers. Hawthorne considered the most symmetrical <u>trans-anti</u> isomers of the dimers were probably obtained, although he had no evidence to prove this.

Two reactions of fully halogenated nitriles CX_3CN($X=F$ or Cl) with diborane have been studied recently.[32] It was found that the reaction at room temperature in the vapour phase was very slow, but at 90-100°C it proceeded much more rapidly giving borazines and polymeric products.

$$3CF_3C{\equiv}N + 1\tfrac{1}{2}B_2H_6 \longrightarrow (CF_3CH_2)_3N_3B_3H_3$$

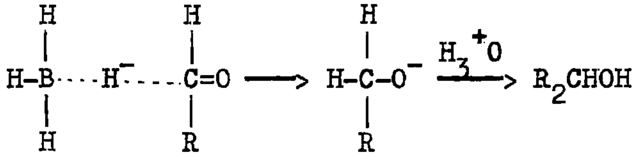
Violent explosions occurred when mixtures of trichloroacetonitrile and diborane were heated in sealed tubes. Explosions were avoided by using tetrahydrofuran or dimethoxyethane as solvents, so that from the reaction trichloroethylideneaminoborane could be isolated:

$$2Cl_3CC{\equiv}N + B_2H_6 \longrightarrow (Cl_3C\text{-}CH{=}N\text{-}BH_2)_n$$

The product melts at 116°C and sublimes under vacuum at 110-120°C. Care is needed, however, since the dry solid explodes on heating. No molecular weight was reported. When the reaction was carried out at a higher temperature the product was $(CCl_3CH_2)_3N_3B_3H_3$, m.p. 202°C.

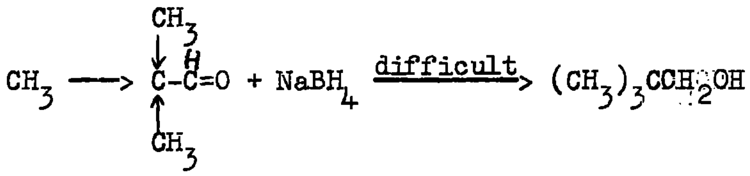
Hydroboration reactions using borohydrides

The mechanism of the reaction of diborane with various functional groups has been discussed above; sodium borohydride appears to react by a slightly different mechanism. Aldehydes and ketones (but not nitriles and olefins) may be reduced in aqueous solvents as there is only slight loss of hydrogen from alkaline solutions.[33] The nucleophilic hydride ion probably attacks the carbon atom of the functional group.

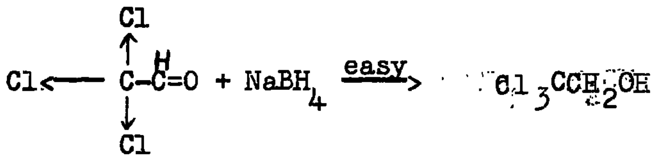


$$\text{H-}\overset{\displaystyle H}{\underset{\displaystyle H}{B}}\cdots H^{-}\cdots\overset{\displaystyle H}{\underset{\displaystyle R}{C}}{=}O \longrightarrow \text{H-}\overset{\displaystyle H}{\underset{\displaystyle R}{C}}\text{-}O^{-} \xrightarrow{H_3{}^{+}O} R_2CHOH$$

This means that in contrast to diborane, sodium borohydride reduces chloral more easily than 2-dimethylpropionaldehyde.[34]



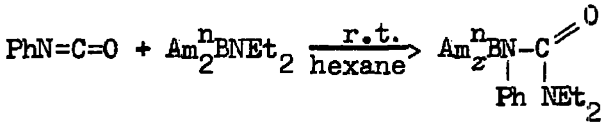
$$CH_3 \rightarrow \overset{CH_3\downarrow}{\underset{\uparrow CH_3}{C}}\text{-}\overset{H}{C}{=}O + NaBH_4 \xrightarrow{\text{difficult}} (CH_3)_3CCH_2OH$$



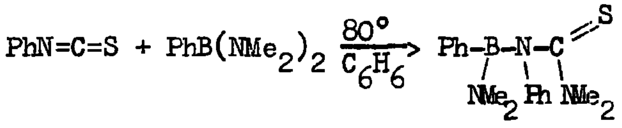
$$Cl \leftarrow \overset{Cl\uparrow}{\underset{\downarrow Cl}{C}}\text{-}\overset{H}{C}{=}O + NaBH_4 \xrightarrow{\text{easy}} Cl_3CCH_2OH$$

Aminoboration

Several workers have shown that an aminoborane group may be added across certain double bonds. The reaction has been particularly well established with isocyanates, and isothiocyanates, the addition going across the azomethine bond.[35]

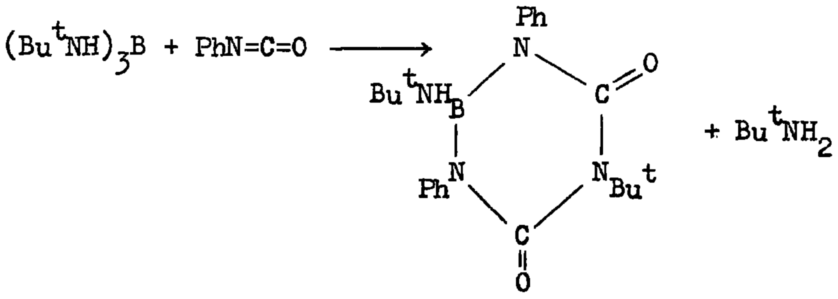


$$PhN{=}C{=}O + Am^n_2BNEt_2 \xrightarrow[\text{hexane}]{\text{r.t.}} Am^n_2B\underset{Ph}{N}\text{-}\underset{NEt_2}{C}{=}O$$

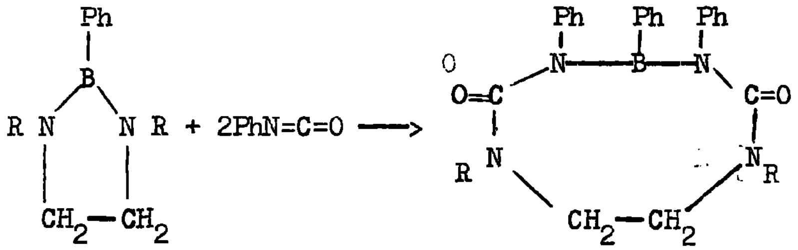


$$PhN{=}C{=}S + PhB(NMe_2)_2 \xrightarrow[C_6H_6]{80°} Ph\text{-}\underset{NMe_2}{B}\text{-}\underset{Ph}{N}\text{-}\underset{NMe_2}{C}{=}S$$

The NHR group moves more readily than the NRR' group:[36]



When the reaction is attempted with cyclic diaminoboranes the product is a larger ring:



Aminoboration reactions have not been observed, however with olefins or acetylenes.[37]

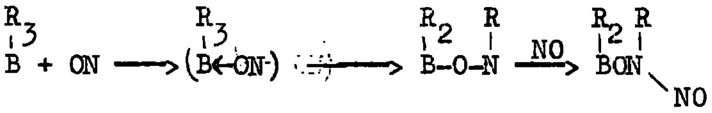
Organoboration

Some reactions of organoboranes with unsaturated molecules are known in which addition of R-B across the multiple bond occurs. The reaction with oxygen is of this type. The formation of a peroxide as the primary (or at least an early) step in the reaction has been confirmed in the case of trimethylborane.[38]

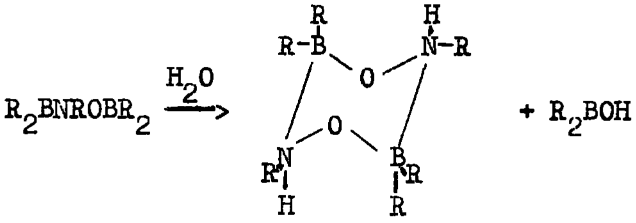
$$Me_3B + O_2 \longrightarrow [Me_3B.O_2] \longrightarrow Me_2BOOMe \longrightarrow MeB(OMe)_2$$

At pressures below the explosion limit Me_2BOOMe is obtained. In a sealed tube at room temperature this rearranges to give 90% dimethoxymethylborane, $MeB(OMe)_2$.

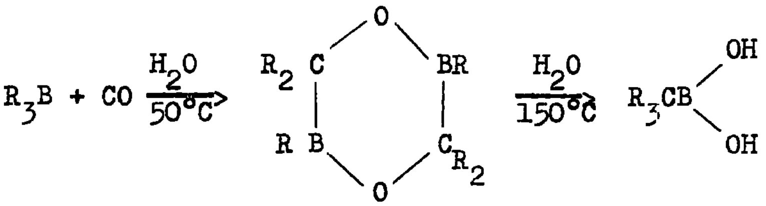
Nitric oxide has been found to react with tri-isobutyl- and triphenylborane.[39] Tri-isobutylborane in cyclohexane takes up two mol. of nitric oxide and triphenylborane takes up 1.6 mol. of nitric oxide both in xylene and cyclohexane. The mechanism suggested is:



A more recent examination of the reaction of nitric oxide with an <u>excess</u> of tributylborane has shown that dibutylaminoxydibutylborane, R_2NOBR_2, and $R_2BNROBR_2$ where R = butyl, are among the products.[40] The presence of these is best explained by a reaction sequence involving the formation of $R_3B.NO$ with a B-N link as the first step. An interesting "Bon-Bon" derivative can be obtained by hydrolysis of the reaction mixture:



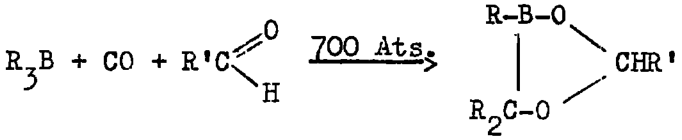
<u>Carbon monoxide</u> reacts with trialkylboranes under pressure in the presence of water to give diboradioxanes:[41]



Similar reactions of trialkylboranes with glycols and carbon monoxide have given cyclic esters of trialkylcarbinylboronic acids.[42]

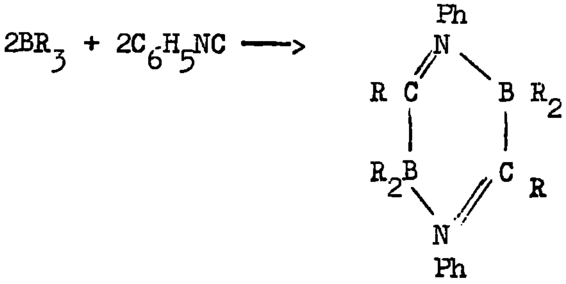
Again an adduct, $R_3B.CO$, appears likely to be involved in the early stages of the reaction. Such an adduct would be expected to be less stable to dissociation than the well known borane carbonyl, $BH_3.CO$, in which the boron-carbon bond is thought to be strengthened by back co-ordination.

In the presence of aldehydes, carbon monoxide and trialkylboranes react under pressure (600-800 ats.) to give boradioxolanes:[43]

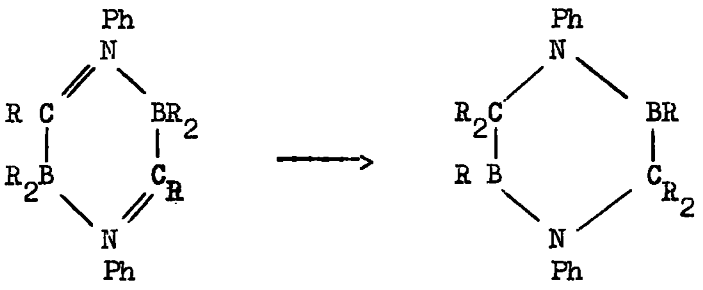


e.g. 4,5,5-triethyl-4-bora-1,3-dioxolane

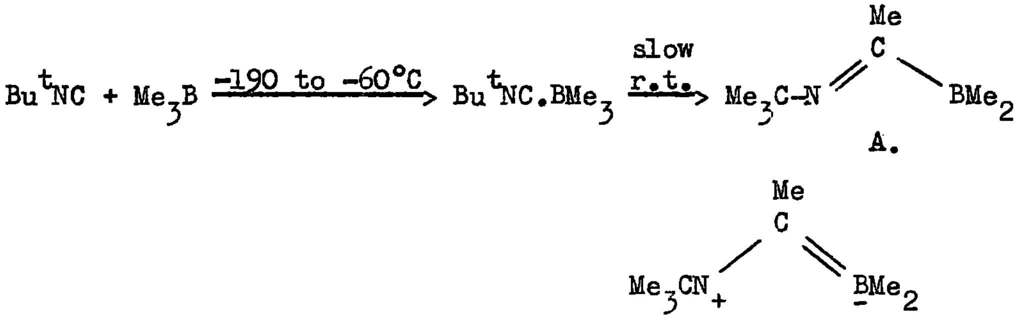
Phenyl isonitrile reacts with trialkylboranes in ether at room temperature to give boron-nitrogen heterocycles:[44]



The infrared spectrum shows strong bands at ca. 1560 $cm.^{-1}$ indicative of the C=N bond. When R was ethyl the compound rearranged rapidly above 200°C into a 2.5.diborapiperazine:



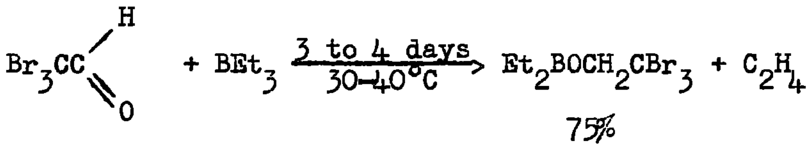
Trimethylborane also reacts with t-butyl isonitrile[45] to give a white crystalline adduct, m.p. 68-70°C. the C≡N frequency in the infrared spectrum occurring at 2247 cm.$^{-1}$ It is thermally unstable and changes by the movement of a methyl group from the boron atom to the carbon atom of the isonitrile group into compound A, m.p. 120°C:



A.

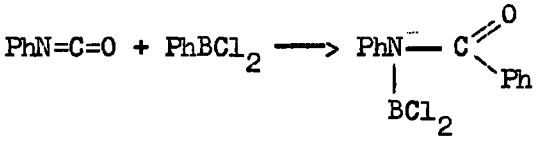
Compound A sublimes slowly at 80-90°C/0.1 mm, is insensitive to air and moisture and is monomeric. Further transfer of a second methyl group from the boron was not reported. The boron-hydrogen analogues were not obtained because the reaction was too vigorous.

In the examples just quoted there has been addition of R-B across an unsaturated molecule. A somewhat different reaction occurs between triethylborane and certain aldehydes when ethylene is evolved and hydrogen is transferred, i.e. a hydroboration reaction occurs. Thus bromal, chloral, benzaldehyde and p-chlorobenzaldehyde react with triethylborane to give esters of diethylboronic acid in 60-90% yields:[46]



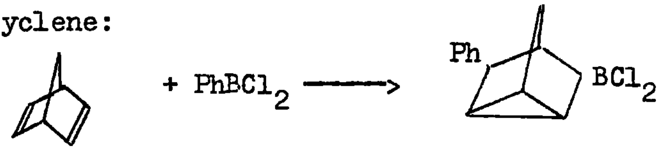
$$Br_3C\overset{H}{C}{=}O + BEt_3 \xrightarrow[30\text{-}40^{\circ}C]{3\text{ to }4\text{ days}} \underset{75\%}{Et_2BOCH_2CBr_3} + C_2H_4$$

Certain arylboron halides can also give organoboration reactions.[47,48] The phenyl-boron group in phenylborondichloride adds across the azomethine bond in phenyl isocyanate:



$$PhN{=}C{=}O + PhBCl_2 \longrightarrow \underset{BCl_2}{PhN}{-}C({=}O)Ph$$

and adds across the double bond in norbornadiene to give cis and trans nortricyclene:

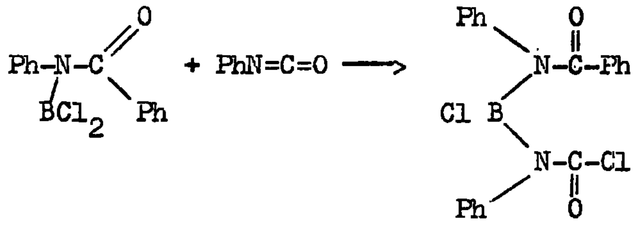


Adducts of the type $RCN.BPhCl_2$, however, do not rearrange on heating.

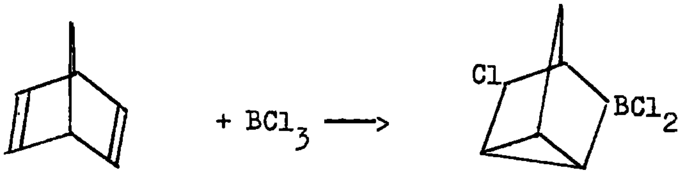
Chloroboration

A few examples are known in which addition of B-Cl to unsaturated molecules occurs. For example, the product of addition of $PhBCl_2$ to

PhNCO can itself add to a further molecule of PhNCO.[49,50]



Norbornadiene will also react with boron trichloride to give the corresponding nortricyclene.

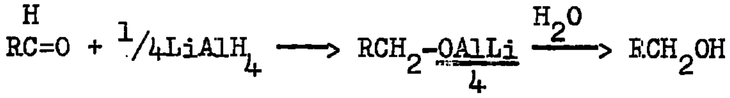


On the whole it is clear that chloroboration occurs less readily than phenylboration and certainly has not the wide application of hydroboration.[51]

Reactions of Aluminium compounds with unsaturated compounds

Lithium aluminium hydride

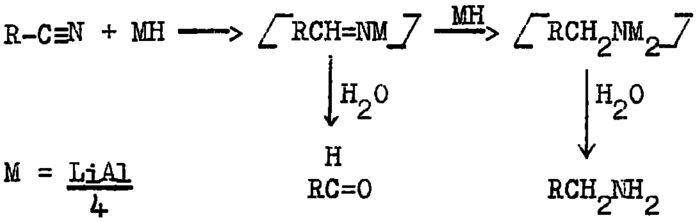
Lithium aluminium hydride has been used extensively for the reduction of unsaturated compounds.[52] The overall reaction involves the addition of Al-H groups across multiple bonds such as C=O and C≡N. It does not react very easily, however, with carbon-carbon double or triple bonds.



$$\overset{H}{RC}=O + {}^{1}/4LiAlH_4 \longrightarrow RCH_2\text{-}\frac{OAlLi}{4} \xrightarrow{H_2O} RCH_2OH$$

The usual procedure is to stir up a slurry of the hydride in diethyl ether, tetrahydrofuran or di-n-butyl ether and add to this the substance to be reduced; hydrolysis of the reaction mixture releases the product. In most cases the reaction produces the lowest reduced state of the functional groups, e.g. nitriles, RCN, give amines, RCH_2NH_2; ketones, R_2CO, give secondary alcohols R_2CHOH, etc.

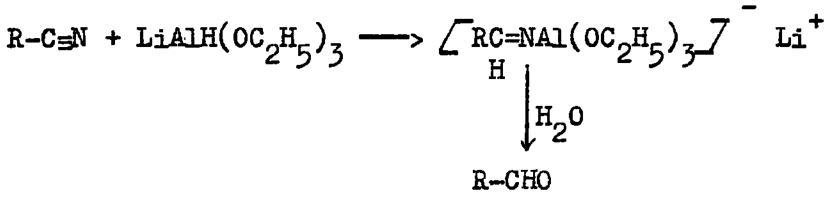
Many nitriles, such as benzonitrile or o-toluonitrile,[53] can be reduced to the corresponding amine in high yield, ca. 80%. As the reaction occurs effectively in two stages, use of a limited amount of hydride results in the formation of a C=N intermediate which on hydrolysis affords the aldehyde:[54]



$$\begin{tikzcd} R\text{-}C\equiv N + MH \arrow[r] & {[RCH{=}NM]} \arrow[r, "MH"] \arrow[d, "H_2O"] & {[RCH_2NM_2]} \arrow[d, "H_2O"] \\ M = \frac{\underline{LiAl}}{4} & \overset{H}{RC{=}O} & RCH_2NH_2 \end{tikzcd}$$

The Al-N intermediates in these reactions have not, however, been isolated.

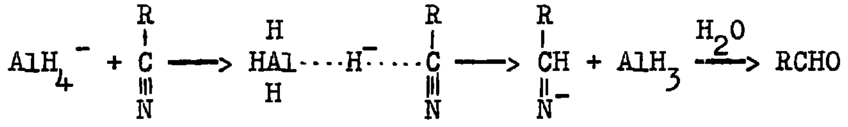
More convenient reagents for the partial reduction of functional groups are the trialkoxy derivatives of lithium aluminium hydride. The product from 3 mol. t-butyl alcohol and lithium aluminium hydride, $LiAl(OC(CH_3)_3)_3H$,[55] has been particularly useful in the reduction of acid chlorides to aldehydes, and lithium[56] and sodium[57,58] triethoxyaluminohydrides have been used for the partial reduction of nitriles to aldehydes. A 100% excess of the alkoxy derivative still does not reduce the C≡N group further.



$$R\text{-}C\equiv N + LiAlH(OC_2H_5)_3 \longrightarrow \left[\underset{H}{RC}{=}NAl(OC_2H_5)_3\right]^- Li^+ \xrightarrow{H_2O} R\text{-}CHO$$

In all these cases separation of the intermediate was not necessary for the isolation of the product.

<u>The mechanism</u> of the reduction using lithium aluminium hydride probably follows a similar pattern to that of lithium borohydride, which it closely resembles in properties and reactions. Lithium aluminium hydride is considered to exist in ether solution largely as ionic aggregates of strongly solvated lithium ions and aluminohydride anions, (AlH_4^-). This being so the hydrogen will probably transfer as hydride in a bimolecular nucleophilic displacement.[59] For example the reduction of nitriles:

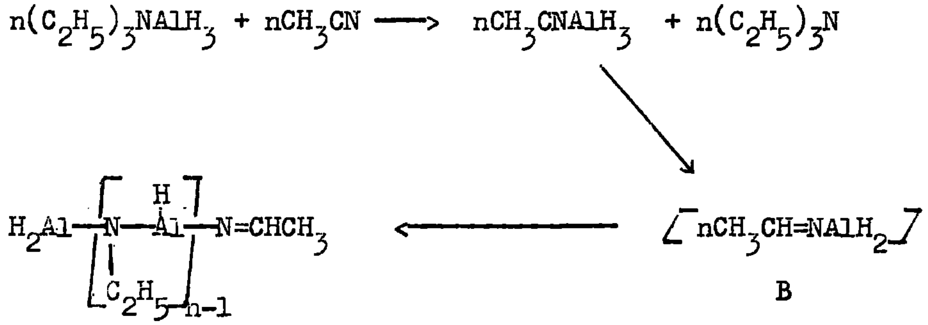


$$AlH_4^- + \begin{matrix}R\\|\\C\\|||\\N\end{matrix} \longrightarrow \begin{matrix}H\\HAl\cdots H^-\cdots\\H\end{matrix}\begin{matrix}R\\|\\C\\|||\\N\end{matrix} \longrightarrow \begin{matrix}R\\|\\CH\\||\\N^-\end{matrix} + AlH_3 \xrightarrow{H_2O} RCHO$$

Aluminium hydride

Recent studies on the reactions of trimethylamine-alane $Me_3N.AlH_3$ with ethylamine, acetonitrile or ethylenimine have shown that polymeric compounds with aluminium-nitrogen chains in them are produced.[60]

The suggested mechanism with acetonitrile is:



$$n(C_2H_5)_3NAlH_3 + nCH_3CN \longrightarrow nCH_3CNAlH_3 + n(C_2H_5)_3N$$

$$H_2Al-\left[\begin{matrix} N & - & \overset{H}{Al} \\ | & & \\ C_2H_5 & & \end{matrix}\right]_{n-1}-N{=}CHCH_3 \longleftarrow [nCH_3CH{=}NAlH_2]$$

A B

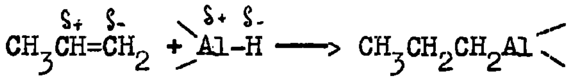
No attempt was made, however, to isolate intermediate B but the product A on hydrolysis gave a trace of ammonia which would be expected to be formed from an ethylideneamino end group. In each case the polymer (molecular weight ca. 2500) was soluble in benzene and had almost exactly one hydrolysable hydrogen atom per aluminium atom.

Organoaluminium hydrides, R_2AlH

Dialkyl aluminium hydrides react with unsaturated molecules by addition of the Al-H group across the multiple bond. Diethylaluminium hydride reacts smoothly with olefins:

$$C_2H_4 + Et_2AlH \longrightarrow Et_3Al$$

Olefins of the type RCH=CHR, e.g. 2-butene, react with Al-H bonds about one hundredth as quickly as 1-olefins.[61] As in hydroboration, the hydrogen atom becomes attached to the more substituted carbon of the olefin:

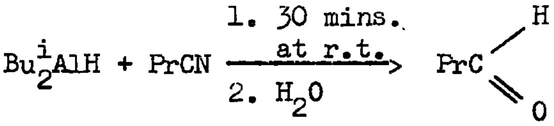


$$CH_3\overset{\delta+}{C}H{=}\overset{\delta-}{C}H_2 + {>}\overset{\delta+}{Al}-\overset{\delta-}{H} \longrightarrow CH_3CH_2CH_2Al{<}$$

This method has been used to prepare mixed trialkyls of aluminium although these usually tend to disproportionate.

$$Et_2AlH + CH_2{=}CMePh \longrightarrow Et_2AlCH_2CHMePr$$

The reaction of di-isobutylaluminium hydride with some nitriles has been investigated.[62] When solutions of di-isobutylaluminium hydride and various cyanides in ether, heptane or benzene were stirred for thirty minutes the products on hydrolysis were the corresponding aldehydes.



However, direct distillation of a mixture of propyl cyanide and di-isobutylaluminium hydride gave butylideneaminodi-isobutylaluminium:

$$PrCN + Bu^i_2AlH \longrightarrow (PrCH{=}NAlBu^i_2)_n, \text{ b.p. } 161^\circ/1 \text{ mm.}$$

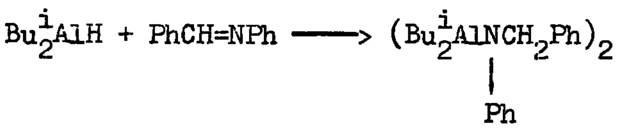
The molecular weight of the product was not recorded.

Tri-isobutylaluminium has been found to react in a similar manner to di-isobutylaluminium hydride in that when 2 mols. are heated with benzonitrile[63] at 80-90°C it evolves 2 mols. isobutylene and benzylamine may be recovered in good yield after hydrolysis of the reaction mixture.

$$PhCN \xrightarrow{Bu^i_3Al} \left[PhCH_2\overset{|}{N}Al<\right]_n \xrightarrow{H_2O} PhCH_2NH_2$$

Similar reactions of $(\mathrm{Bu}^i)_3\mathrm{Al}$ and $\mathrm{Bu}^i_2\mathrm{AlH}$ with aldehydes and ketones have given good yields of the corresponding alcohols.[64,65]

A further reaction of dibutylaluminium hydride has shown that the Al-H group will add across the azomethine bond in benzylideneaniline:[66]



$$\mathrm{Bu^i_2AlH + PhCH{=}NPh \longrightarrow (Bu^i_2Al}\underset{\mathrm{Ph}}{\underset{|}{\mathrm{N}}}\mathrm{CH_2Ph)_2}$$

That the resulting coloured solution no longer contained molecules with C=N bonds was shown by the absence of a band around 1600 cm.$^{-1}$ in the infrared spectrum.

Organoaluminium compounds other than $\mathrm{Bu}^i_3\mathrm{Al}$, have been shown to lose olefins and react with certain aldehydes as if they were organoaluminium hydrides, $\mathrm{R_2AlH}$. For example, triethylaluminium reduces chloral in a similar way to triethylborane with the elimination of ethylene:[67]

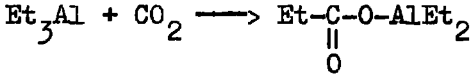
$$\mathrm{Et_3Al + 3CCl_3CHO \longrightarrow (CCl_3CH_2O)_3Al + 3C_2H_4}$$

Aluminium trialkyls

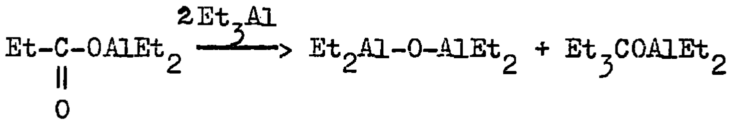
Aluminium trialkyls react with various multiply bonded groups by addition of R-Al across the multiple bond. For example they react with oxygen smoothly forming aluminium alkoxides.[68,69,70] Two thirds of the total oxygen absorbed is taken up rapidly and the final third rather slowly because the initial product, as in the case of the boron alkyls, is a peroxide,[71,72,73] formed by addition of R-Al across the oxygen molecule:

$$>\text{Al-R} + \text{O}_2 \longrightarrow\ >\text{Al-O-OR} \xrightarrow{>\text{AlR}} 2>\text{AlOR}$$

Carbonation of triethylaluminium gives at first diethylaluminium propionate.[68,74]

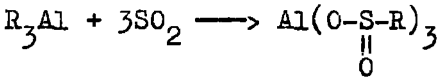

$$\text{Et}_3\text{Al} + \text{CO}_2 \longrightarrow \text{Et-}\underset{\underset{\text{O}}{\parallel}}{\text{C}}\text{-O-AlEt}_2$$

Hydrolysis of the product gives propionic acid. When an excess of triethylaluminium is used the reaction proceeds further:


$$\text{Et-}\underset{\underset{\text{O}}{\parallel}}{\text{C}}\text{-OAlEt}_2 \xrightarrow{2\text{Et}_3\text{Al}} \text{Et}_2\text{Al-O-AlEt}_2 + \text{Et}_3\text{COAlEt}_2$$

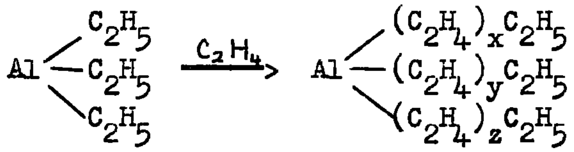
Hydrolysis in this case gives triethylcarbinol.

Reaction of the trialkyls with sulphur dioxide[74] gives addition across one of the S=O bonds leaving aluminium salts of sulphinic acids:


$$\text{R}_3\text{Al} + 3\text{SO}_2 \longrightarrow \text{Al(O-}\underset{\underset{\text{O}}{\parallel}}{\text{S}}\text{-R)}_3$$

Dinitrogen tetroxide has been found to react with triethylaluminium etherate in ether to give a yellow brown solution which on hydrolysis yields N,N-diethylhydroxylamine, Et_2NOH.[75] In a similar reaction nitric oxide apparently gave ethylnitrosohydroxylamine, EtN(NO)OH, which may have been formed via an adduct, NOAlEt_3 (cf. NOBR_3).

Aluminium trialkyls react with α-olefins[4] in the temperature range 100-200°C, often giving a mixture of products,



$$Al\begin{cases} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{cases} \xrightarrow{C_2H_4} Al\begin{cases} (C_2H_4)_xC_2H_5 \\ (C_2H_4)_yC_2H_5 \\ (C_2H_4)_zC_2H_5 \end{cases}$$

from which a mixture of straight chain hydrocarbons can be obtained on hydrolysis.

Various workers[76,77] have reported that trialkyls of aluminium add across acetylenic triple bonds.

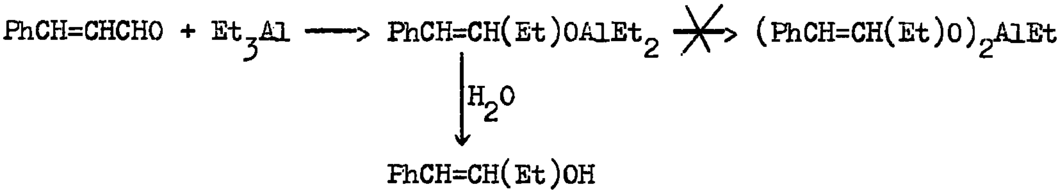
$$(C_2H_5)_3Al + CH{\equiv}CH \longrightarrow (C_2H_5)_2AlCH{=}CHC_2H_5$$

$$(C_2H_5)_3Al + PhC{\equiv}CH \longrightarrow (C_2H_5)_2AlCH{=}CPhC_2H_5$$

However, as acetylene itself or its monosubstituted derivatives RC≡CH contain acidic hydrogen atoms, elimination of alkanes R'H might also occur in reactions with aluminium trialkyls, R'_3Al. A recent study[78] of several monosubstituted acetylenes has shown that such elimination reactions do in fact occur rather than the addition reactions reported by other workers.[76,77]

$$PhC{\equiv}CH + Et_3Al \longrightarrow PhC{\equiv}CAlEt_2 + EtH$$

In the reactions of aluminium trialkyls with <u>aldehydes</u> and <u>ketones</u>, after one of the alkyl groups has been transferred to the carbon atom of the C=O group the remaining two alkyl groups do not add to other C=O groups:



$$\begin{tikzcd}
PhCH{=}CHCHO + Et_3Al \arrow[r] & PhCH{=}CH(Et)OAlEt_2 \arrow[r, "\times" marking] \arrow[d, "H_2O"] & (PhCH{=}CH(Et)O)_2AlEt \\
& PhCH{=}CH(Et)OH &
\end{tikzcd}$$

However, in most cases loss of olefin occurs and addition of Al-H is the result, as already described.[46]

Acid chlorides react readily with aluminium trialkyls. The reaction cannot be used for ketone synthesis because the ketone produced is itself susceptible to further attack by the trialkyl:

$$AlR'_3 + RCOCl \longrightarrow R'_2AlCl + RR'CO \xrightarrow{AlR'_3} RR'_2COAlR'_2$$

Several workers, however, have found that dialkylaluminium chlorides and alkylaluminium dichlorides react with acid chlorides smoothly to give the corresponding ketones:[79,80]

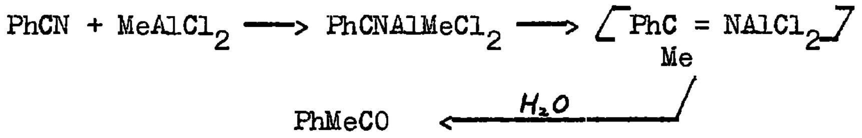
$$R_2AlCl + ClCOR' \longrightarrow RAlCl_2 + RCOR'$$

The reaction with dialkylaluminium chloride stops at this stage because the products are in the form of a stable adduct which is unreactive towards an excess of acid chloride. Also dialkylaluminium chlorides do not add across the carbonyl group of ketones.[81] However uncomplexed alkylaluminium dichlorides will react with acid chlorides:[82]

$$RAlCl_2 + ClCOR' \longrightarrow RCOR' + AlCl_3$$

Nitriles

Reactions with phenyl cyanide have shown that addition across the C≡N bond will take place.[83] A mixture of phenyl cyanide and methylaluminium dichloride heated for 12 hours at 170°C gave, on hydrolysis, a 39% yield of acetophenone:



$$\mathrm{PhCN + MeAlCl_2 \longrightarrow PhCNAlMeCl_2 \longrightarrow [\underset{Me}{PhC} = NAlCl_2]}$$

$$\mathrm{PhMeCO \xleftarrow{H_2O}}$$

Methyl and ethyl cyanides gave much lower yields of ketone (4-9%) since methane gas is lost on heating with methylaluminium dichloride, presumably because of the acidity of these nitriles:

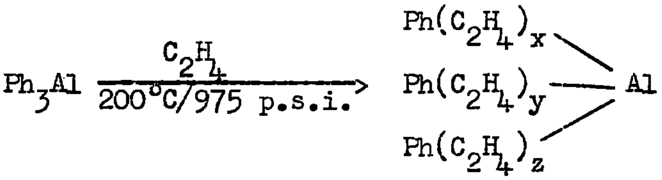
$$\mathrm{MeAlCl_2 + CH_3CN \longrightarrow [Cl_2AlCH_2CN]_n + CH_4}$$

Better yields were obtained with dimethylaluminium chloride but again the yields from the alkyl cyanides (<u>ca</u>. 10%) were much lower than from phenyl cyanide (up to 60% depending upon the conditions used for the reaction). No intermediates were isolated.

<u>Arylaluminium compounds</u>

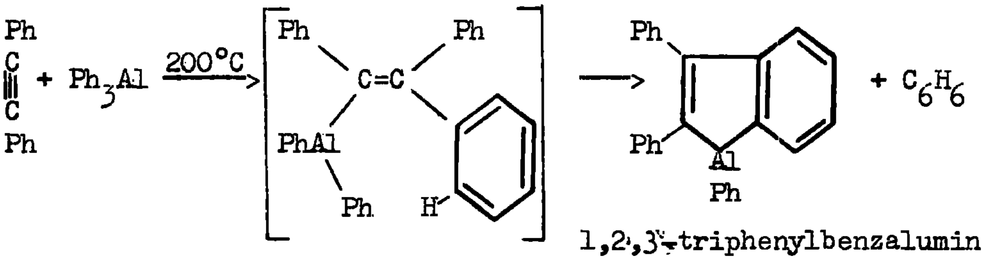
The addition reactions of triarylaluminium compounds are similar to those of the trialkyls but tend to occur less readily and in some instances are more complicated. Thus, in contrast to the aluminium alkyls, the reaction with oxygen is slow and complex.[84] Oxygenation of an ethereal solution of triphenylaluminium gave phenol, acetophenone, and acetaldehyde among the products evidently by attack on the solvent, possibly by a mechanism involving free radicals.

Ethylene, on the other hand, reacts with triphenylaluminium in the same way as it reacts with triethylaluminium,[84]



producing on hydrolysis a mixture of phenylalkanes.

The addition of triphenylaluminium across an acetylenic triple bond has been used in the synthesis of an aluminium heterocycle:[85]



1,2',3'-triphenylbenzaluminole

m.p. 286°C.

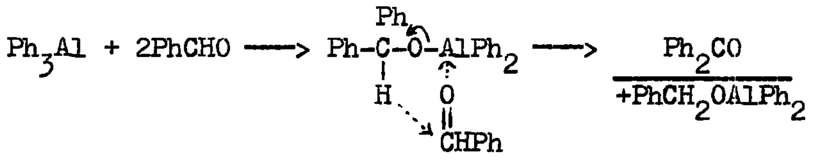
Reactions with carbonyl groups

Carbon dioxide has been shown to react with some difficulty with aluminium triaryls to give the aryl carboxylic acid on hydrolysis:[86]

$$(pMeC_6H_4)_3Al \xrightarrow[\text{2. } H_2O]{\text{1. } CO_2\text{, boiling xylene, 2 hours}} 3pMeC_6H_4COOH$$

Experiments on the reactions of aldehydes and ketones generally gave the expected products although often in low yields as other reactions took place simultaneously. Benzaldehyde and triphenylaluminium give in addition to the expected diphenylcarbinol significant quantities of benzophenone and benzyl alcohol, which can be accounted for by reactions of the following type:[87]

$$Ph_3Al + 3PhCHO \longrightarrow (Ph_2CHO)_3Al \xrightarrow{H_2O} \underline{3Ph_2CHOH} \qquad 27\%$$



$$Ph_3Al + 2PhCHO \longrightarrow Ph\text{-}\overset{Ph}{\underset{H}{C}}\text{-}O\text{-}AlPh_2 \longrightarrow \begin{array}{c}\underline{Ph_2CO}\\ +PhCH_2OAlPh_2\end{array} \qquad 30\%$$

$$PhCH_2OAlPh_2 \xrightarrow{H_2O} \underline{PhCH_2OH} \qquad 29\%$$

It has been found that triphenylaluminium and <u>phenyl cyanide</u> react to form an adduct, $PhCN.AlPh_3$, which does <u>not</u> rearrange in refluxing benzene[88] whereas tri-p-tolylaluminium and phenyl cyanide after being heated in boiling xylene for 30 minutes gave, on hydrolysis, a 17% yield of phenyl-p-tolylketone:[86]

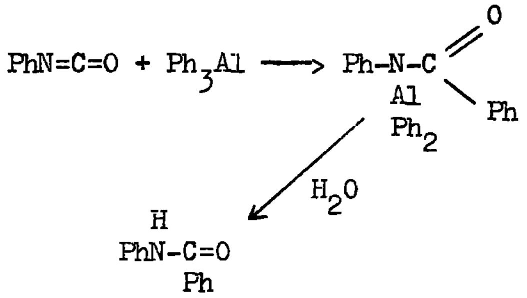
$$\begin{tikzcd}
PhCN + (p\text{-}MeC_6H_4)_3Al \arrow[r] & \left[p\text{-}MeC_6H_4CPh{=}NAl(p\text{-}MeC_6H_4)_2\right] \arrow[d, "H_2O"] \\
 & PhCOC_6H_4Me
\end{tikzcd}$$

The C=N intermediate was not isolated. But more recently, since the present work was started, examples of this type of intermediate have been reported by other workers,[89] for example, $(Ph_2C{=}NAlPh_2)_{1.1}$ m.p. 295°C (from PhCN and Ph_3Al at 220°C) and $(C_{10}H_7(Ph)C{=}NAlPh_2)_{1.5}$ (from $C_{10}H_7CN$ and Ph_3Al). Two phenyl groups remained attached to the aluminium and further rearrangement to

$(Ph_2RCNAlPh)_n$ did not occur even when the products were heated to 350°C, when benzene was evolved.

$$PhCN + Ph_3Al \xrightarrow{220^\circ C} (Ph_2C{=}NAlPh_2)_{1.1}$$

Phenyl isocyanate has also been shown to react with triphenyl- and tri-p-tolylaluminium to give on hydrolysis benzanilide and p-tolyl-anilide[86]



cf. The reaction of phenylboron dichloride with phenyl isocyanate, see page 22.

Addition compounds of nitriles

A large number of addition compounds, $RCN \rightarrow MX_n$, of nitriles with various Lewis acids has been prepared.[90,91,92,93] Some examples of these, where MX_n is borane BH_3, or derivatives thereof or an organoaluminium compound have been described already (see pp. 12,13) in connection with their occurrence as intermediates in certain addition reactions, e.g.

$$RCN + B_2H_6 \longrightarrow RCN.BH_3 \longrightarrow [RCH{=}NBH_2]_n \longrightarrow (RCH_2NBH)_3$$

Most of the known adducts of nitriles have halides as the acceptor molecules. These adducts are usually prepared by mixing the reactants neat or in an inert solvent and further purification, if necessary, is effected by sublimation or recrystallisation. They are generally sensitive to hydrolysis by moisture necessitating handling under an inert or at least dry atmosphere. The persistence of bands in the C≡N region shows that the adducts are correctly described by the formula $RC\vdots N.MX_n$ and that rearrangement to $RC(X):N.MX_{n-1}$ has not occurred. In the following table a selection of these adducts is listed together with their C≡N stretching frequencies. In the third column the difference in frequency of the C≡N band in the adducts from that of the free nitrile appears.

Table 1

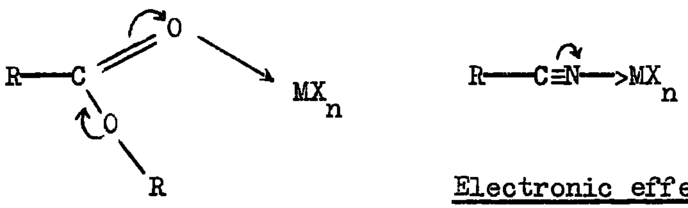
The C≡N stretching frequencies of some nitrile adducts

Compound	ν(C≡N) frequency cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$
MeCN	2253[94,95]	
$MeCN,BF_3$	2359[90]	106
$MeCN,BCl_3$	2357[90]	104
$MeCN,AlBr_3$	2335[95]	82
$MeCN,AlCl_3$	2330[95]	77
$MeCN,SnCl_4$	2330[95]	77
$MeCN,BBr_3$	2320[92]	67

Table 1 (cont'd)

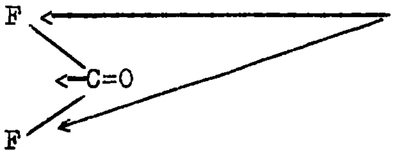
Compound	ν(C≡N) frequency cm.$^{-1}$	$\Delta\nu$ Cm.$^{-1}$
$(MeCN)_2,TiCl_4$	2304[90]	51
$(MeCN)_2,SnCl_4$	2303[90]	50
$MeCN,BH_3$	2280[29]	27
PhCN	2229[92]	
$PhCN,BF_3$	2336[90]	107
$PhCN,BCl_3$	2317[90] 2304[92]	88
$(PhCN)_2,TiCl_4$	2270[90]	41
$(PhCN)_2,SnCl_4$	2254[90]	25

In the many examples of complexes $RR'C{=}O.MX_n$ formed between compounds containing carbonyl groups (e.g. aldehydes, ketones, acid chlorides or amides, esters etc.) and Lewis acids the carbonyl frequency is lowered[96] and this is often used to determine whether co-ordination involves the carbonyl group in compounds containing other possible donor atoms, e.g. acid chlorides or amides. This lowering of the frequency is thought to be the sum of two opposing effects whose magnitudes are not known, (a) the lowering of the bond order (and force constant) by co-ordinate bond formation,



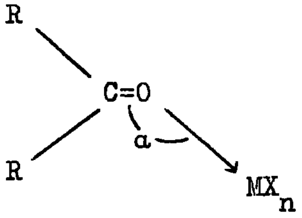
Electronic effect of co-ordination upon C=O and C≡N bond orders

and (b) a raising of the frequency by a mechanical effect. Overend and Scherer[97] calculated that the force constants of the C=O bonds in carbonyl halides COX_2 were equal whereas the difference between the C=O stretching frequencies in COF_2 and $COCl_2$ was 100 $cm.^{-1}$ This may be explained by assuming that the strong C-F bonds hinder movement of the carbon atom along the line of the C=O bond and thus increase the apparent strength of the C=O bond. This results in higher vibrational energy for the C=O bond and a correspondingly higher frequency in the infrared spectrum.



strength of these bonds prevent the C atom moving so easily.

A similar effect occurs in complexes of ketones or nitriles. In ketones, for example, the co-ordinate bond is generally of low force constant and is at about 120° to the C=O and therefore the interaction to raise the frequency is low. However, when a linear complex is formed, as with nitriles the mechanical effect offsets any electronic effects (assuming that these lower the C≡N bond order) to such an extent that the C≡N frequency is <u>raised</u> by as much as 100 cm.$^{-1}$ as can be seen from Table 1.



effect of this bond on the easy
movement of the O atom small,
as ∠α ≏ 120°.

$R—C≡N \rightarrow MX_n$

greater effect because
∠CNM = 180°.

The increase in the C≡N stretching frequency on co-ordination has been explained in another way.[92] It has been suggested that the C≡N bond order in the complexes is in fact <u>higher</u> than that in the free nitriles, in which the CN bond may be intermediate between a double and a triple bond:[98]

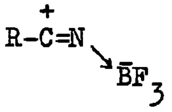
$$\text{i.e.}\quad RC{\equiv}N\!:\ \longleftrightarrow\ R\text{-}\overset{+}{C}{=}\overset{-}{\bar{N}}$$

sp hybridisation of N. sp^2 hybridisation of N.

The directions in which a dative link can be formed would differ in these two canonical forms; the former giving rise to a linear complex, the latter to an angular complex:

$$\text{i.e.}\quad R\text{-}C{\equiv}\overset{+}{N}\rightarrow\overset{-}{B}F_3$$

A (sp)



$$R\text{-}C{=}\overset{+}{N}\searrow\bar{B}F_3$$

B (sp^2)

That the linear structure A is correct has been shown by a complete structural analysis of the acetonitrile-boron trifluoride complex,[99] in which ∠CCN = 180°, ∠CNB = 180° and the CN bond length (1.13Å) is slightly less than that in the free nitrile (1.16Å), although the difference is just outside the mean deviations.

Discussion

Discussion

The Reaction of methyl cyanide with tetramethyldiborane and related compounds

In the introduction it was mentioned that diborane had been shown to react with methyl cyanide to form a crystalline solid adduct, $MeCN\rightarrow BH_3$, which decomposed at 20°C to form N'N"N"'triethylborazine, $(EtNBH)_3$, together with more highly polymeric materials.[29] The reaction apparently proceeded by stepwise transfer of two hydrogen atoms from the boron atom to the carbon atom of the cyanide group, as originally proposed by Burg:[28]

$$MeC{\equiv}N,BH_3 \longrightarrow (MeCH{=}NBH_2)_n \longrightarrow (MeCH_2N{=}BH)_m$$

The only evidence obtained for the ethylidene intermediate, $(MeCH{=}N.BH_2)_n$, was spectroscopic. A small quantity of material, detected by its infrared spectrum, showed a strong absorption band at 1685 $cm.^{-1}$ which might have been due to a C=N vibration.

The object of this present investigation was to determine whether a stable ethylideneaminoboron compound could be prepared. The method chosen was to use 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:

$$MeC{\equiv}N,BHR_2 \longrightarrow (MeCH{=}N.BR_2)_n$$

Alkyl groups were used as the unreactive groups after it was found that trimethylborane and triethylborane did not react with methyl cyanide at temperatures up to 100°C.

Since this work was started two reports have appeared of compounds of this type. Hawthorne has shown that it is unnecessary to start with a <u>di</u>alkylborane, BHR_2, in order to prepare stable alkylideneaminoboranes since he found that trimethylamine t-butylborane, Me_3N,BH_2Bu^t would react with various nitriles, RCN, to give stable alkylideneamino-t-butylboranes $(RCH{=}N.BHBu^t)_2$.[31]

It has also been found that from a reaction of trichloroacetonitrile and diborane in tetrahydrofuran trichloroethylideneaminoborane $(CCl_3CH{:}NBH_2)_n$, m.p.116°C. could be isolated.[32]

$$Cl_3CC{\equiv}N + B_2H_6 \longrightarrow (Cl_3CCH{=}NBH_2)_n \longrightarrow (CCl_3CH_2NBH)_3$$

The product explodes when heated. Its molecular weight was not recorded.

The dialkyl boranes, BHR_2, investigated in the present work were the tetraalkyldiboranes, $Me_2BHBHMe_2$ and $Et_2BHBHEt_2$, and the unsymmetrical dialkyldiboranes, Me_2BHBH_3 and Et_2BHBH_3. The tetraalkyldiboranes reacted slowly at room temperature with methyl cyanide to form materials identified on the evidence discussed below as the ethylideneaminodialkylboranes $(MeCH{=}NBMe_2)_2$ and $(MeCH{=}NBEt_2)_2$ respectively. These same products were isolated after the reaction of the dialkyldiboranes with methyl cyanide, together with N'N"N"' triethylborazine and some involatile viscous liquids, similar to those formed by reaction of diborane with methyl cyanide. It was therefore evident that the reactions which had occurred were:

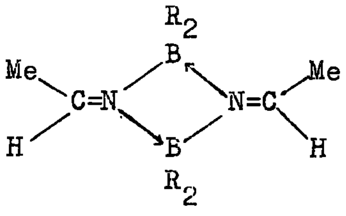
$$2MeC\equiv N + R_2BHBHR_2 \longrightarrow (MeCH{=}NBR_2)_2$$

and $$2MeC\equiv N + R_2BHBH_3 \longrightarrow {}^1/2(MeCH{=}NBR_2)_2 + \frac{1}{n}(MeCH_2NBH)_n$$

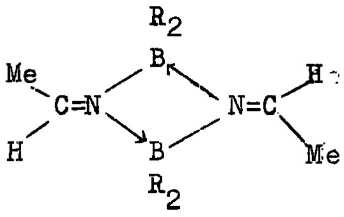
No evidence was obtained of an adduct $MeC\equiv N,BHR_2$, in which hydrogen transfer had not occurred, although such a material may have been formed transiently during the reaction.

The ethylideneaminodialkylborane dimers were characterised as follows. Full elemental analysis and molecular weights, determined cryoscopically in benzene solution, confirmed the formulae $(C_4H_{10}BN)_2$ and $(C_6H_{14}BN)_2$ for the products derived respectively from tetramethyldiborane and tetraethyldiborane. A strong band in their infrared spectra at about 1695 $cm.^{-1}$ was good evidence for the presence of a C=N band in the molecule. This conclusion was supported by the formation of ammonia, not ethylamine, on reaction of the compounds with strong alkali at above 100°C, and by the isolation of acetaldehyde 2,4-dinitrophenylhydrazone when the samples were boiled with dilute acid and the vapours were passed into a solution of 2,4-dinitrophenylhydrazine. Reaction with an excess of water vapour at 105°C for 1 day gave the appropriate dialkylborinic acid and an involatile yellow residue. When ethylideneaminodimethylborane was heated with an excess of hydrogen chloride at 105°C for two days it gave dimethylchloroborane, methyldichloroborane, trimethylborane and an involatile amorphous solid.

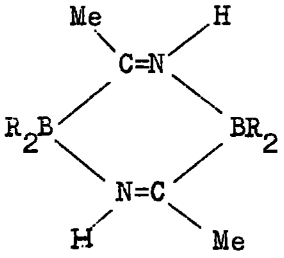
All this evidence was consistent with an ethylideneaminodialkylborane formula, $(MeCH{=}NBR_2)_2$, where R=Me or Et, and the structure Ia or Ib, cis and trans isomers differing in the relative orientation of their ethylidene groups:



Ia



Ib



II

An alternative explanation in terms of structure II was ruled out by further infrared spectroscopic evidence. The spectra showed only very weak bands at about 3400 cm.$^{-1}$ which were better explained as overtones of the very strong bands at 1695 cm^{-1}, rather than as N-H stretching bands, while a band at 3000 cm^{-1} could be assigned to the C-H stretching vibration of a group =CMe-H.

Both _cis_ and _trans_ isomers of structure I might be expected to be formed in the reaction studied, and in the case of ethylideneaminodimethylborane dimer, $(\mathrm{MeCH{=}N.BMe_2})_2$, two isomers were obtained and separated by vacuum distillation. The two products were a colourless crystalline solid, v.p. 0.6 mm. at 20°C, m.p. 76°C and a colourless liquid v.p. 1.8 mm. at 20°C, m.p. _ca_. -5°C. Both of these isomers were dimeric in the gas phase at 100-150°C or in benzene solution, and their infrared spectra were very similar, see figure 1 . Each isomer could be recovered unchanged after vacuum distillation at room temperature and essentially unchanged after heating to 150°C, although both decomposed when heated to 155°C for 18 hours. No evidence was obtained for the conversion of one isomer into the other via thermal dissociation into a monomeric form, $\mathrm{MeCH{=}N\overset{\rightarrow}{=}BMe_2}$: the products of thermal decomposition included involatile yellow viscous liquids, small quantities of trimethylborane, and traces of unidentified materials which yielded more trimethylborane on treatment with concentrated sulphuric acid.

It seems most reasonable that the isomer having the lower melting point and higher volatility has the _cis_ structure Ia, and

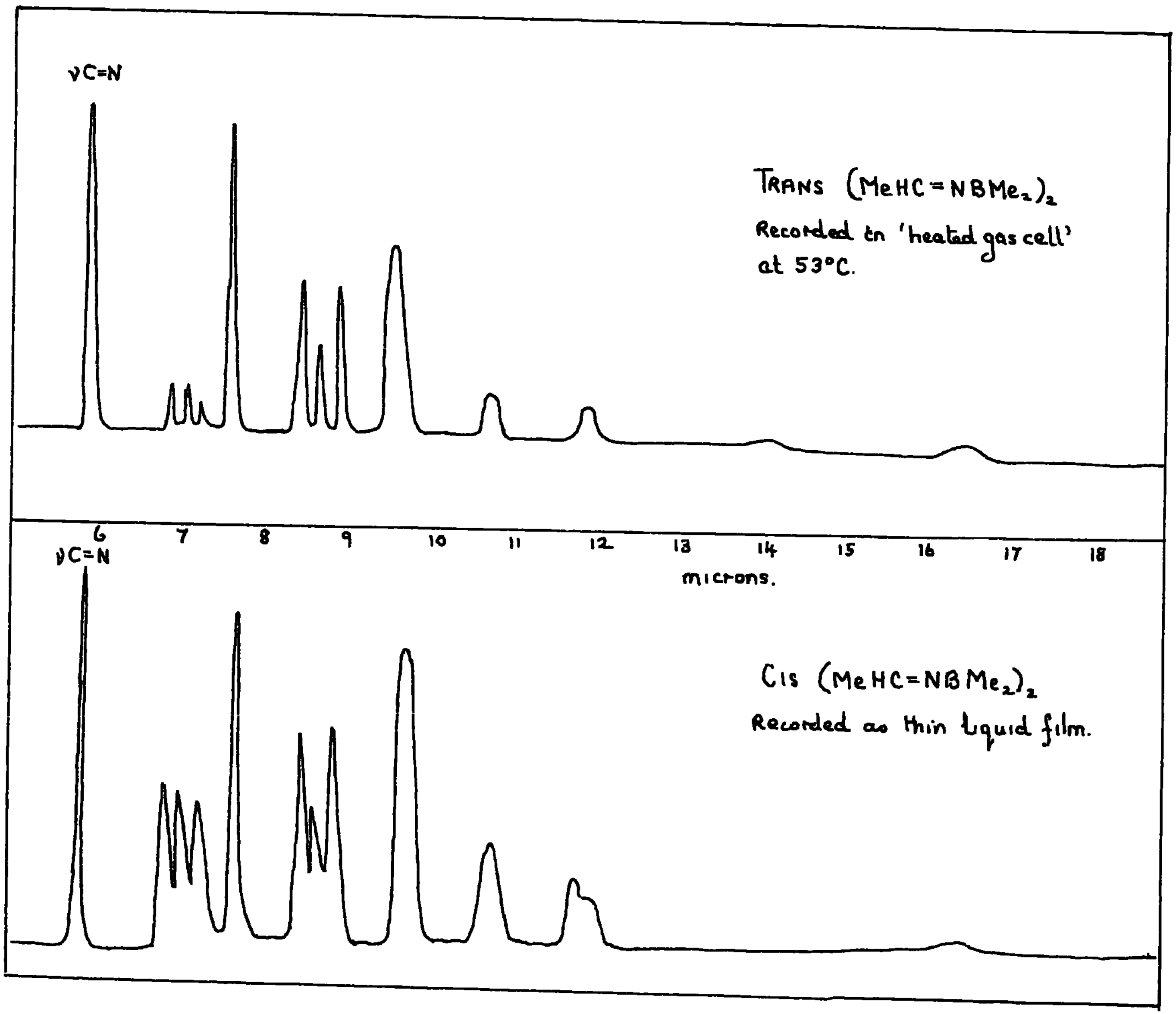
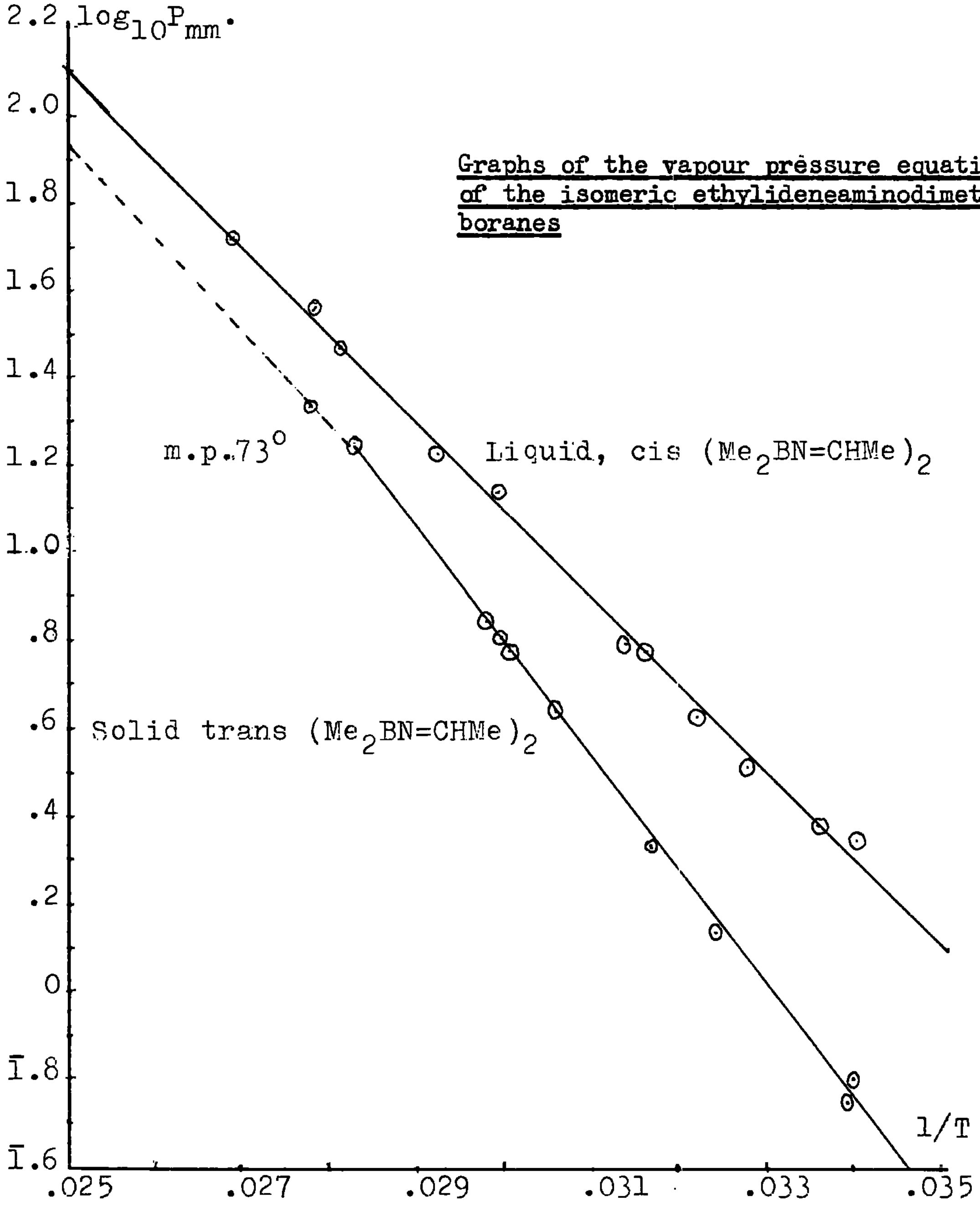
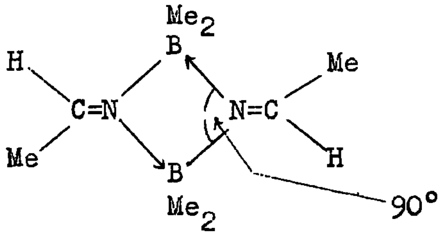


Figure 1

The infrared spectra of the isomeric ethylideneaminodimethylborane dimers

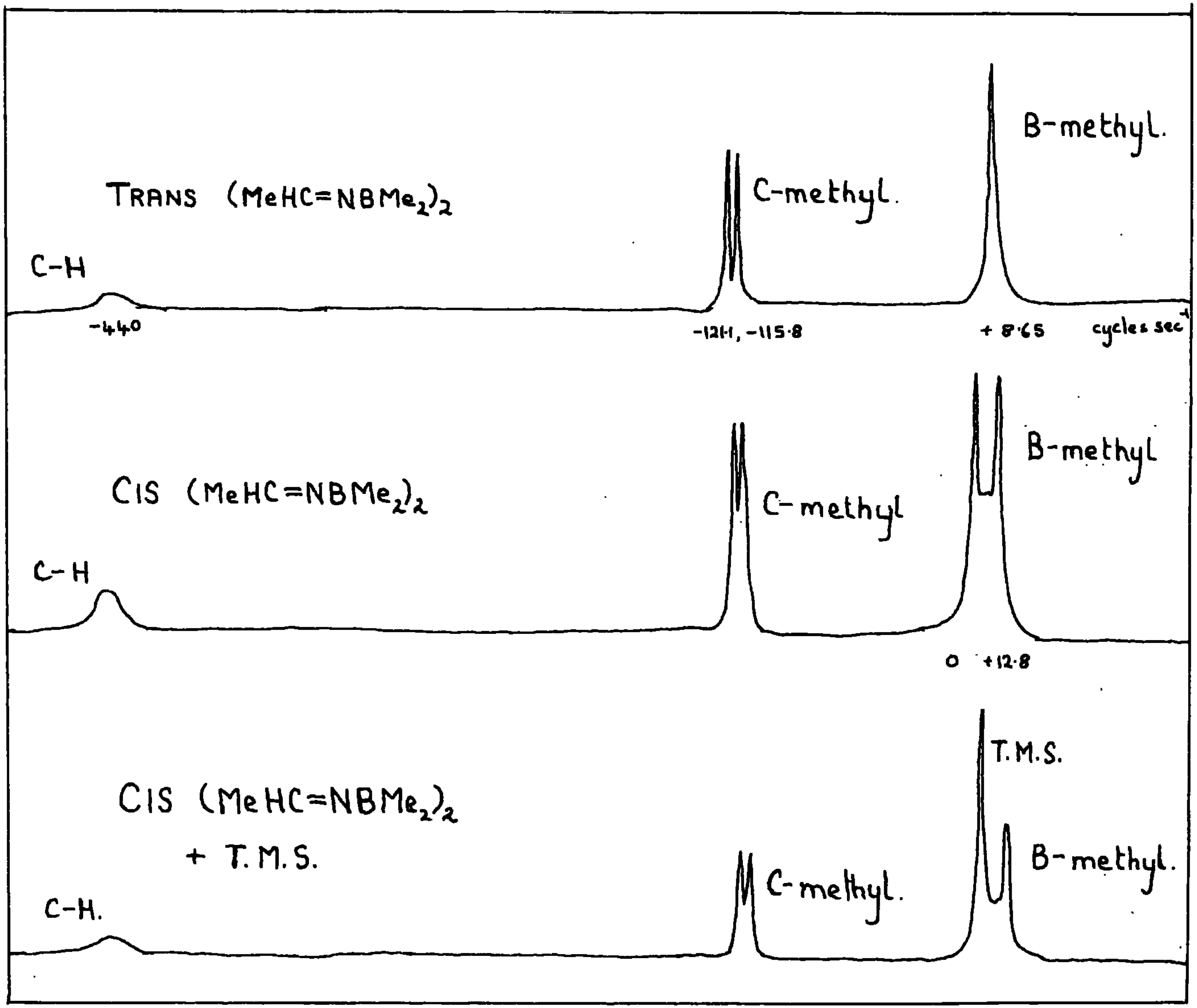


Graphs of the vapour pressure equations of the isomeric ethylideneaminodimethylboranes the crystalline solid has the trans structure Ib. The volatilities of the two isomers are very close at the melting point of the solid (see p.) but at -18°C the difference was great enough to allow the cis isomer to be removed from the solid trans isomer, which was virtually involatile at this temperature. Dr. H.M.M. Shearer and Miss J. Willis of these laboratories are carrying out an X-ray crystallographic study of the crystalline solid isomer. Observations have shown the crystals to be monoclinic, of space group $P2_1/a$, with unit cell dimensions a = 6.55, b = 11.92, c = 7.89 Å, β = 105° 23', and with four $MeCH{=}NMe_2$ units in the unit cell. Further investigation which is not yet complete indicates the ∠BNB in the boron-nitrogen four membered ring to be 90° ± 5°.



The trans arrangement of the ethylidene groups about the four-membered ring is supported by the X-ray crystallographic evidence.

The nuclear magnetic resonance spectra in carbon tetrachloride of both the liquid and the solid isomers were recorded on an A.E.I. R.S.2. spectrometer operating at 60 Mc/s. The spectrum of the solid isomer is consistent with the structure Ib in that it shows four peaks whose positions ~~are~~ relative to an internal reference of tetramethylsilane, and relative intensities (shown in parenthesis) are -442.0 (2), -121.1 (3), -115.8 (3) and +8.65 (12) cycles $sec.^{-1}$ Positive values are to higher applied magnetic fields than the reference signal. The two sharply defined peaks each of intensity 3 can be attributed to the methyl groups attached to carbon atoms, which are spin-spin coupling to a single hydrogen nucleus. The separation between the two peaks gives J_{CH_3-H} = 5.3 cycles $sec.^{-1}$, which may be compared with the values of 5.3 to 6.3 cycles $sec.^{-1}$ found in the oximes and various substituted hydrazones of acetaldehyde.[100] The peak at the lowest field is a broad single peak (width at half-height 20 c/s) which from its intensity can be assigned to the two hydrogen nuclei. The width of this peak is evidence for structure I rather than II since the CH peaks in I would give a 1:3:3:1 quartet from spin-spin coupling with the CH_3 hydrogen nuclei on the same carbon atom, and each component of the quartet would be broadened by the effect of the ^{14}N nuclear quadrupole moment, so that the peak would be an unresolved broad peak of width 20 cycles $sec.^{-1}$ The N-H peaks in structure II would also show a quartet structure, but the effect of quadrupolar broadening by the ^{14}N nucleus in this case would most probably broaden the peaks beyond the limits of detection. The peak at highest applied field is broad and single, and arises from the four methyl groups attached to the boron atoms. A single peak for these methyl groups supports the structure Ib

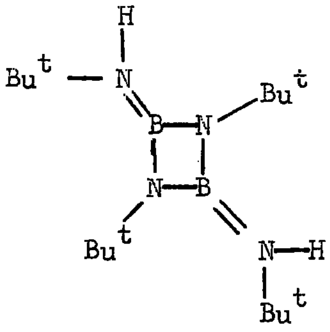


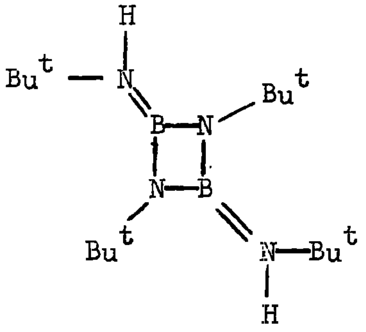
The proton nuclear magnetic resonance spectra of the isomeric ethylideneaminodimethylboranes for the solid compound since in this structure the B-methyl groups have an identical environment and are magnetically equivalent, whereas structure Ia should give rise to two B-methyl peaks in the n.m.r. spectrum.

The spectrum of the liquid isomer as a dilute solution in carbon tetrachloride is identical with that of the solid isomer, except that there are two high field peaks arising from the B-methyl hydrogen nuclei; these are of equal intensity and are at 0.0 and +12.8 cycles $sec.^{-1}$ from tetramethylsilane. The presence of two B-methyl peaks is consistent with structure Ia for the liquid isomer, as in this structure two B-methyl groups have only C-methyl neighbours through space and the other two have only C-H neighbours; hence a chemical shift is expected between the B-methyl resonances.

It was not found possible to separate the dimeric ethylideneaminodiethylboranes, $(MeCH{=}NBEt_2)_2$, melting range -18 to -10°C, into isomers by vacuum distillation at room temperature, nor by vapour phase chromatography using nitrogen as carrier gas over silicone elastomer. The isomers which were presumably present, judging by the melting range of the compound, apparently differed less in their vapour pressures than did their methyl analogues. The ethyl groups on the boron atom make the n.m.r. spectrum too complicated to interpret with any certainty.

As has been mentioned in the introduction the possibility of cis-trans isomerism was commented on by Hawthorne in describing the dimeric alkylideneamino-t-butylboranes $(RCH{=}NBHBu^t)_2$.[31] He considered the products most likely to be formed would be the <u>trans-anti</u> isomers although he was unable to show unambiguously whether his products were single or mixed isomers. Lappert and Majumdar have obtained spectroscopic evidence for a similar type of isomerism involving a 4-membered boron-nitrogen ring with exocyclic double bonds to the boron atoms in the compound 1,3-di-t-butyl-2,4-t-butylamino-1,3-diaza-2,4-boretane.[101]





but again no isomers were separated.

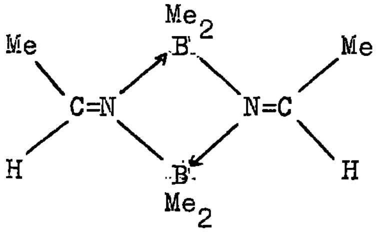
Attempts to prepare monomeric ethylideneaminodiethylborane, $MeCH{=}N{\rightleftarrows}BEt_2$ by thermal dissociation of the dimer were unsuccessful. Prolonged pyrolysis of $(MeCH{=}NBEt_2)_2$ led to products similar to those obtained from $(MeCH{=}NBMe_2)_2$ i.e. some triethylborane, an involatile yellow viscous liquid and an unidentified fraction which may have been an amine adduct of triethylborane.

An attempt to replace the B-methyl groups by fluorine by a reaction of solid $(MeCH{=}NBMe_2)_2$ with boron trifluoride did not lead to any easily identifiable products. The gas left in the bulb showed bands attributable to B-Me groups in the infrared spectrum but it appeared that the reaction had broken down the ethylideneamino compound so that no simple products were formed.

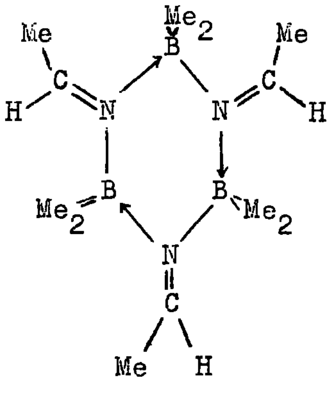
The dimeric nature of the ethylideneaminoboranes deserves further comment. It was considered possible that monomeric, dimeric or trimeric species might have been obtained, A, B or C.

$\mathrm{MeHC{=}N\overset{\rightarrow}{=}BMe_2}$

A



B



C

It is most commonly found that compounds of the type $R_2BNR'_2$ achieve co-ordinative saturation by forming dimers, rather than exist as monomers with a double N⇌B bond.[102] The exact reason for this is not clear. The factors which prevent association are bulky groups R and R' which sterically hinder dimerisation, or aromatic groups which, by giving rise to π-bonding in the aryl-B bond, apparently reduce co-ordinative unsaturation at the boron atom.

As in the alkylideneaminoboranes the attached groups are neither bulky (the C=N ensuring that alkylidene group is remote from the rings) nor aromatic, dimerisation occurs. This dimer, B, must involve some strain since the angles of the bonds at the boron atoms are reduced from the 109° tetrahedral angle to <u>ca</u>. 90° and the angles at the nitrogen atoms are reduced from the 120° trigonal angle also to about 90°. For this reason a trimeric form C, where angles nearer to 109° and 120° could be accommodated, might have been expected. However, six membered rings $(R_2BNR'_2)_3$ are rare. The attached substituent groups R and R' are more crowded in such compounds than in the dimers $(R_2BNR'_2)_2$ and the only examples known have been prepared by addition reactions of borazines, in which the six-membered ring is already present.

Reactions of nitriles with organo-aluminium compounds

As described in the introduction, nitriles, RCN, react with organo-aluminium compounds, R'_3Al, to form adducts $RCN \rightarrow AlR'_3$ which rearrange when heated to form alkylideneaminoaluminium compounds, $(RR'C{:}N.AlR'_2)_2$ similar to the ethylideneaminoboranes just discussed. When RCN is acetonitrile, an alternative decomposition reaction can occur with the formation of materials of the type $(R'_2AlCH_2CN)_n$. In the following pages the evidence for the occurrence of these reactions in the present investigation will be discussed. A discussion of the formation of the adducts is followed by a consideration of their thermal decomposition. Some aspects of the infrared and nuclear magnetic resonance spectra of the rearranged materials are also discussed.

Nitrile adducts of organo-aluminium compounds.

Adducts $RCN\text{-}AlR'_3$ were prepared by direct reaction between appropriate quantities of nitrile and organo- aluminium compound. The compounds prepared in this way are listed in Table **2** , i.e. the 1.1 adducts of methyl or phenyl cyanide with trimethyl-, triethyl-, and triphenylaluminium, and dimethylaluminium chloride.

The particular method used varied slighly according to the reactivity and volatility of the reactants. Thus trimethylaluminium was transferred into the reaction vessel by condensation under vacuum whereas triphenylaluminium ether complex was tipped into the vessel under nitrogen. The alkyl aluminium adducts were all purified by vacuum sublimation and the triphenylaluminium adducts by recrystallisation from methylcyclohexane. The adducts were all sensitive to air but especially the alkyls which fumed vigorously in moist nitrogen. Acid hydrolysis was used as the method of analysing these compounds because this established that no rearrangement involving movement of groups R' from aluminium had taken place.

$$RCN.AlR'_3 + 5H_2O \longrightarrow RCOONH_4 + 3R'H + Al(OH)_3$$

$$RCN.AlR'_2Cl + 5H_2O \longrightarrow RCOOH + NH_4Cl + 2R'H + Al(OH)_3$$

Molecular weight measurements indicated that all the adducts were monomeric. The infrared spectra also confirmed these formulae, as opposed to $RC(R')=NAlR'_2$, in that medium or strong intensity absorption bands occurred in the region of C≡N stretching vibrations.

The frequencies of the C≡N bands are listed in Table 2 and may be compared to those of nitrile groups in the halide addition compounds listed in Table 1 in the introduction, p.36.

Table 2

The C≡N stretching frequencies in adducts of nitriles with alkyl- and aryl- aluminium compounds

Compound	m.p.	ν(C≡N) cm.$^{-1}$	Δν cm.$^{-1}$
MeCN		2253	
MeCN,$AlMe_2Cl$	73°	2299	46
MeCN,$AlMe_3$	73°	2295	42
MeCN,$AlEt_3$	-6°	2290	37
MeCN,$AlPh_3$	138°	2275	22
PhCN		2229	
PhCN,$AlMe_2Cl$	83°	2284	55
PhCN,$AlMe_3$	80°	2275	46
PhCN,$AlEt_3$	liq.	2270	41
PhCN,$AlPh_3$		2266	37

It is immediately apparent that the shift in the CN frequency on co-ordination to organo-aluminium compounds is less than the corresponding shift on co-ordination to halide acceptors. If the Al-N and C≡N bonds in adducts $RC{\equiv}N{\rightarrow}AlX_3$ are considered, then strengthening of the Al$\leftarrow$N bond would prevent free movement of the nitrogen atom, as discussed in the introduction. Thus the C≡N stretching frequency should increase with the strength of the Al-N link. This appears to be the case. Dimethylaluminium chloride would be expected to be the best acceptor of the compounds examined because the electronegative chlorine atom withdraws electrons from the aluminium. This shows in that the highest frequency occurs in the dimethylaluminium chloride adducts in both the MeCN and PhCN series.

Trimethylaluminium would also be expected to be a slightly better acceptor than triethylaluminium, in view of the relative inductive effects of the methyl and ethyl groups and also for steric reasons, but a poorer acceptor than dimethylaluminium chloride. This, too, shows up in the nitrile frequencies since the trimethyl- and triethylaluminium adducts of both methyl- and phenyl cyanide have smaller shifts in frequency than the dimethylaluminium chloride adducts and the nitrile frequency of the trimethylaluminium adducts is slightly greater than in those of triethylaluminium.

The triphenylaluminium adducts would appear to have the weakest Al-N bonds since both the methyl cyanide and phenyl cyanide complexes show the lowest frequencies.

The strength of the Al-N bond is considered to be the major factor in determining the sequence $\nu_{C\equiv N}(Me_3Al.NCR) > \nu_{C\equiv N}(Et_3Al.NCR) > \nu_{C\equiv N}(Ph_3Al.NCR)$ as the <u>mechanical effect</u>, discussed in the introduction (p.37) which is related to the mass of the group AlR_3, would lead to the reverse order.

The aluminium-nitrogen stretching frequencies could not be measured since they occurred at too low a frequency for them to be recorded by the instrument used, so it is not possible to check this argument by comparing the Al-N stretching frequencies of the adducts.

The thermal decomposition of the nitrile adducts

As the adducts tended to decompose by one or more of three main types of reaction, the types will be outlined at this point before a more detailed treatment of individual reactions.

Methyl and phenyl cyanides were chosen as representatives of the alkyl and aryl series which had an important difference. This was the acidity of the hydrogen atoms in methyl cyanide which was not present in phenyl cyanide. The phenyl cyanide adducts reacted to form the rearranged compounds in good yields, although movement of a second organic group was not observed:

$$(1) \quad PhCN + R_3Al \longrightarrow (PhRC{=}NAlR_2)_n \longrightarrow (PhCR_2NAlR)_m$$

The rearrangement reactions of the methyl cyanide adducts were complicated because of the acidity described above so that as well as reaction (1), loss of hydrocarbon could occur:

$$(2) \quad CH_3CN + R_3Al \longrightarrow (R_2AlCH_2CN)_n + RH$$

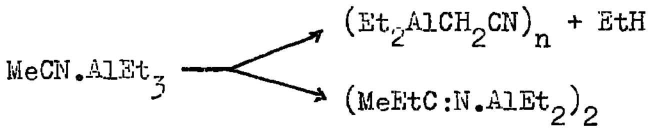
This was in fact the major reaction when alkyl cyanide adducts were thermally decomposed.

The aluminium compounds used were trimethyl- triethyl- and triphenylaluminium, dimethylaluminium hydride and dimethylaluminium chloride. The trimethyl and triphenyl compounds and dimethylaluminium chloride reacted at elevated temperatures (100-250°C) to give rearranged materials by movement of an organic group. Dimethylaluminium hydride reacted immediately at room temperature by addition of the Al-H group across the $C\equiv N$ bond:

$$MeCN + Me_2AlH \longrightarrow (MeHC{=}NAlMe_2)_2$$

It appears from the reaction temperatures that the order of decreasing ease of movement of the groups used is $H > Me > Et > Ph$, and that the methyl groups in dimethylaluminium chloride migrate less readily than those in trimethylaluminium.

Triethylaluminium adducts could undergo two types of rearrangement reaction, one involving movement of an ethyl group, the other involving loss of ethylene and subsequent movement of hydrogen. The former type of reaction was shown by the methyl cyanide adduct, from which some $(MeEtC{=}NAlEt_2)_2$ was recovered after thermal decomposition:



$$MeCN.AlEt_3 \rightarrow (Et_2AlCH_2CN)_n + EtH \quad ; \quad MeCN.AlEt_3 \rightarrow (MeEtC{:}N.AlEt_2)_2$$

On the other hand, the phenyl cyanide adduct decomposed with loss of ethylene:

$$2PhCN.AlEt_3 \longrightarrow (PhHC{:}N.AlEt_2)_2 + 2C_2H_4$$

A reaction of this latter type was already known to occur between Bu^i_3Al and PhCN, involving in this case loss of butene and formation of a residue which on hydrolysis afforded benzylamine, $PhCH_2NH_2$.[63]

The decomposition of the phenyl cyanide adducts

The rearrangement reactions of the phenyl cyanide adducts had fewer complications than those of methyl cyanide and generally gave better yields of the rearranged material $(PhRC{=}NAlR_2)_2$. The results are summarised in Table 3 .

Table 3

Thermal decomposition of phenyl cyanide adducts: reaction conditions and products

Compound	Reaction temp. °C.	Time for reaction	Yield and Product
$PhCNAlMe_3$	160-170°C	4 hours	> 50% $(PhMeC{=}NAlMe_2)_2$
$PhCNAlEt_3$	at 190°C sudden loss of C_2H_4		75% $(PhHC{=}NAlEt_2)_2$
$PhCNAlPh_3$	sublimed at 240°C/0.01 mm. giving		15% $(Ph_2C{=}NAlPh_2)_n$
	(boiling xylene	4 hours)	see reference 89
$PhCNAlMe_2Cl$	170-180°C	20 hours	60% $(PhMeC{=}NAlMeCl)_2$
$PhCN + AlMe_2H$	Room temp.	Immediate	> 90% $(PhHC{=}NAlMe_2)_2$

The adducts rearranged smoothly at elevated temperatures as can be seen from the table except for that of triethylaluminium. This adduct darkened slowly on heating until at 190°C a sudden rush of ethylene occurred and a dark viscous liquid frothed up in the flask, which yielded benzylideneaminodiethylaluminium $(PhCH{:}NAlEt_2)_2$ when distilled under vacuum. Dimethylaluminium hydride, in contrast to the other compounds reacted immediately at room temperature by addition of Al-H across the C≡N bond.

The compounds were analysed for hydrolysable alkane or benzene and for aluminium.

$$\tfrac{1}{n}(RR'C{=}NAlR'_2)_n \xrightarrow{H_2O} RR'C{=}O + NH_3 + Al(OH)_3 + 2R'H$$

The molar ratio of alkane or benzene to aluminium was 2:1 for all the compounds, except $(PhMeC{=}NAlMeCl)_2$ which was 1:1, showing that they had rearranged. $(PhMeC{=}NAlMeCl)_2$ was also analysed for nitrogen and chlorine.

Hydrolysis of the compounds by dilute acid gave the appropriate aldehyde or ketone which was identified by its 2,4-dinitrophenylhydrazone or phenylhydrazone.

Hydrolysis with alkaline solution gave ammonia identified by its infrared spectrum.

The molecular weights, measured cryoscopically in benzene showed all of the rearranged compounds to be dimeric, except $Ph_2AlN{=}CPh_2$ which was insoluble. A recent report of this compound gives its degree of association measured ebullioscopically in benzene as 1.1.[89]

The infrared spectra of the compounds in the range 4000-450 cm.$^{-1}$ are listed in the experimental section. One of the most prominent features is the C=N stretching frequency which occurred in each as a strong band at about 1630 cm,$^{-1}$ see Table 5.

The decomposition of the methyl cyanide adducts

The reactions of the methyl cyanide adducts $MeCN.AlR_3$ were complicated in that the predominant reaction was loss of hydrocarbon

RH leaving a brown solid, approximating in composition to $(R_2AlCH_2CN)_n$.

$$MeCN + R_3Al \longrightarrow (R_2AlCH_2CN)_n + RH$$

Simultaneously, rearrangement reactions leading to alkylideneamino derivatives $(MeRC{:}N.AlR_2)_2$ also took place; these alkylideneamino products could be sublimed or distilled in vacuum from the less volatile and clearly more polymeric brown solids.

The results, including one reaction with ethyl cyanide, are summarised below in Table 4 .

Table 4

Thermal decomposition of methyl cyanide adducts: reaction conditions and products

Compound	Reaction temp. °C.	Time	Gas evolved (moles gas/ mole adduct)	Products and Yield
$MeCNAlMe_3$	150	5 hours	CH_4 0.59	$(Me_2C{=}NAlMe_2)_2$ 19% + brown solid
$MeCNAlEt_3$	110	1 hour	C_2H_6 0.51	$(MeEtC{=}NAlEt_2)_2$ 18% + brown solid
$MeCNAlPh_3$	sublimed at 200°/.01 mm.		little C_6H_6	$(MePhC{=}NAlPh_2)_n$ 15% + brown solid

Table 4 (cont'd)

Compound	Reaction temp. °C.	Time	Gas evolved (moles gas/ mole adduct)	Products and Yield
$MeCNAlMe_2Cl$	165	20 mins.	CH_4 0.97	$(Me_2C{=}NAlMeCl)_2$ + liq. 7%)brown solid 2%)solid
$MeCN + Me_2AlH$	Room Temp.	Immediate	None	$(MeHC{=}NAlMe_2)_{2-3}$ >90%
$EtCNAlMe_3$	170	1 hour	CH_4 0.39	$(EtMeC{=}NAlMe_2)_2$ 26% + brown solid

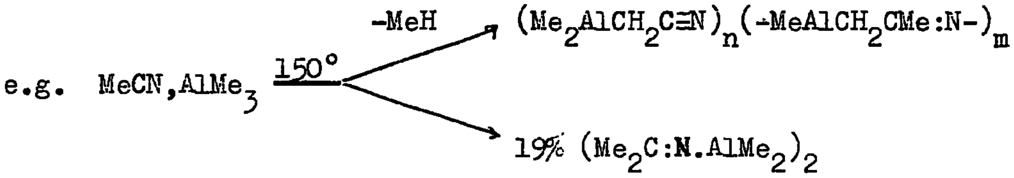
The reactions with trimethylaluminium were carried out in sealed tubes. It was found that at temperatures below 120°C methane was evolved slowly and the amount of product $(Me_2AlN{=}CMe_2)_2$ was small; at 150°C the best yield (19%) of the rearranged material was obtained. When triethylaluminium-methyl cyanide adduct was heated in a flask there was a sudden rush of ethane at 110°C (if large quantities of material are used precautions must be taken to prevent the gas from blowing the apparatus apart) but when the temperature was increased slowly to 200°C very little more ethane came off and at 210°C under vacuum dimeric s-butylideneaminodiethylaluminium, $(MeEtC{=}NAlEt_2)_2$ distilled out.

Dimethylaluminium chloride-methyl cyanide adduct was allowed to react at various temperatures. Below 160°C methane was evolved slowly but little rearranged material was formed and heating the adduct at 210°C in a sealed tube only gave a black solid and methane. However, if the adduct was heated slowly to 165°C there was a sudden rush of methane and a brown solid was left from which a colourless solid could be sublimed and a liquid distilled when it was heated under vacuum. Both the colourless solid and the liquid have the same analytical composition corresponding to $(Me_2C{=}NAlMeCl)_n$; the molecular weight of the liquid corresponded to the dimer (n = 2), but the solid was too insoluble for molecular weight measurements to be carried out. The overall yield of products agrees with figures given by Pasynkiewicz et al. who obtained about 10% of acetone on hydrolysis of the reaction mixture from a similar experiment.[83]

The triphenylaluminium adduct when heated evolved a small amount of benzene and gave a low yield of a colourless sublimate $(PhMeC{=}NAlPh_2)_n$.

Dimethylaluminium hydride reacted with methyl cyanide immediately at room temperature with no evolution of gas. When the product was distilled under vacuum, however, the colourless distillate slowly turned yellow and solidified.

It is evident from these results that the two reactions (a) to form rearranged materials and (b) to evolve gases occur at similar temperatures.



$$\text{e.g. } MeCN,AlMe_3 \xrightarrow{150^\circ} \begin{cases} \xrightarrow{-MeH} (Me_2AlCH_2C{\equiv}N)_n(-MeAlCH_2CMe{:}N-)_m \\ \longrightarrow 19\%\ (Me_2C{:}N.AlMe_2)_2 \end{cases}$$

<u>The rearranged compounds</u> were analysed in the same way as the related compounds prepared from phenyl cyanide i.e. for hydrolysable alkane or benzene and aluminium.

$$\tfrac{1}{2}(RR'C{=}NAlR'_2)_2 \xrightarrow{H_2O} RR'C{=}O + NH_3 + Al(OH)_3 + 2R'H$$

$$\tfrac{1}{2}(RHC{=}NAlR'_2)_2 \xrightarrow{H_2O} RHC{=}O + NH_3 + Al(OH)_3 + 2R'H$$

The ratio of methane, ethane or benzene to aluminium was 2:1 for all the compounds except that from dimethylaluminium chloride which was 1:1. Some were also analysed for nitrogen.

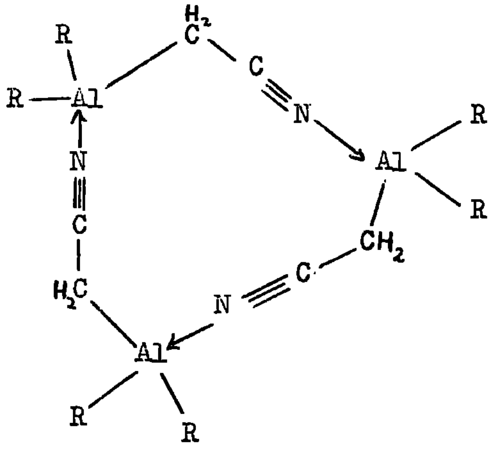
Hydrolysis of the compounds with dilute acid gave the corresponding aldehydes or ketones which were identified as 2,4-dinitrophenylhydrazones.

Hydrolysis with dilute alkali gave ammonia gas which was identified by its infrared spectrum.

Molecular weight determinations carried out cryoscopically in benzene showed most of the compounds to be dimeric; although the results for $(MeHC{=}NAlMe_2)_n$ corresponded to values of n between 2 and 3. The compound $(\mathrm{MePhC{=}NAlPh_2})_n$ and the solid $(\mathrm{Me_2C{=}NAlMeCl})_n$ (from MeCN,$\mathrm{AlMe_2Cl}$) were too insoluble for measurements to be carried out.

<u>The residue</u> in these reactions was not fully investigated but analysis for hydrolysable organic groups and aluminium showed the molar ratio of these to be between 1:1 and 2:1. The infrared spectra had broad peaks in the C≡N region but because of the highly coloured nature of the material the rest of the spectrum had too high a background to pick out a C=N band. The compounds were generally insoluble in benzene and ether which suggests that they are polymeric, probably containing the units $(\mathrm{R_2AlCH_2C{\equiv}N{\rightarrow}})_n$ and $(\mathrm{RAlCH_2{-}\overset{R}{C}{=}N{-}})_n$.

It is possible that a trimer of $(\mathrm{R_2AlCH_2C{\equiv}N{-}})_n$ could be formed:



However, since the residue was found to be insoluble in all the solvents tried, sublimation was left as the only means of separation of such a trimer. This was impracticable since the temperature needed for sublimation would be high enough to allow a second group, R, to move which would break down the ring structure.

Hydrolysis of the material from MeCN.AlMe$_3$ produced some acetone which must have come from the second type of structure:

$$\frac{1}{n}(.\mathrm{MeAlCH_2CMe{=}N.})_n \xrightarrow{H_2O} \mathrm{MeH} + \mathrm{Al(OH)_3} + \mathrm{NH_3} + \mathrm{Me_2CO}$$

The infrared spectra of the rearranged compounds, listed in the experimental section, in full, showed strong bands at about 1650 cm.$^{-1}$ which are listed in Table 5.

Table 5

Infrared spectra

The C=N and Al-N stretching frequencies in compounds of the type

$(\mathrm{RR'C{=}NAlR''_2})_n$

Compound	Frequency ν(C=N) cm.$^{-1}$	ν(Al-N) cm.$^{-1}$
$(\mathrm{MePhC{=}NAlMe_2})_2$	1634	?
$(\mathrm{PhHC{=}NAlEt_2})_2$	1633	468
$(\mathrm{PhHC{=}NAlMe_2})_2$	1630	470
$(\mathrm{MePhC{=}NAlMeCl})_2$	1619	443
$(\mathrm{Ph_2C{=}NAlPh_2})_n$	1595	481
$(\mathrm{Me_2C{=}NAlMe_2})_2$	1656	465
$(\mathrm{MeEtC{=}NAlMe_2})_2$	1659	473
$(\mathrm{MeEtC{=}NAlEt_2})_2$	1650	472

Table 5 (cont'd)

Compound	Frequency ν(C=N) cm.$^{-1}$	ν(Al-N) cm.$^{-1}$
$(Me_2C{=}NAlMeCl)_2$, liq.	1651	479
$(MeHC{=}NAlMe_2)_n$	1690	457
$(PhMeC{=}NAlPh_2)_n$	1621	461

In the spectrum of $(MeHC{=}NAlMe_2)_n$ there was also a band of medium intensity at 1640 cm.$^{-1}$

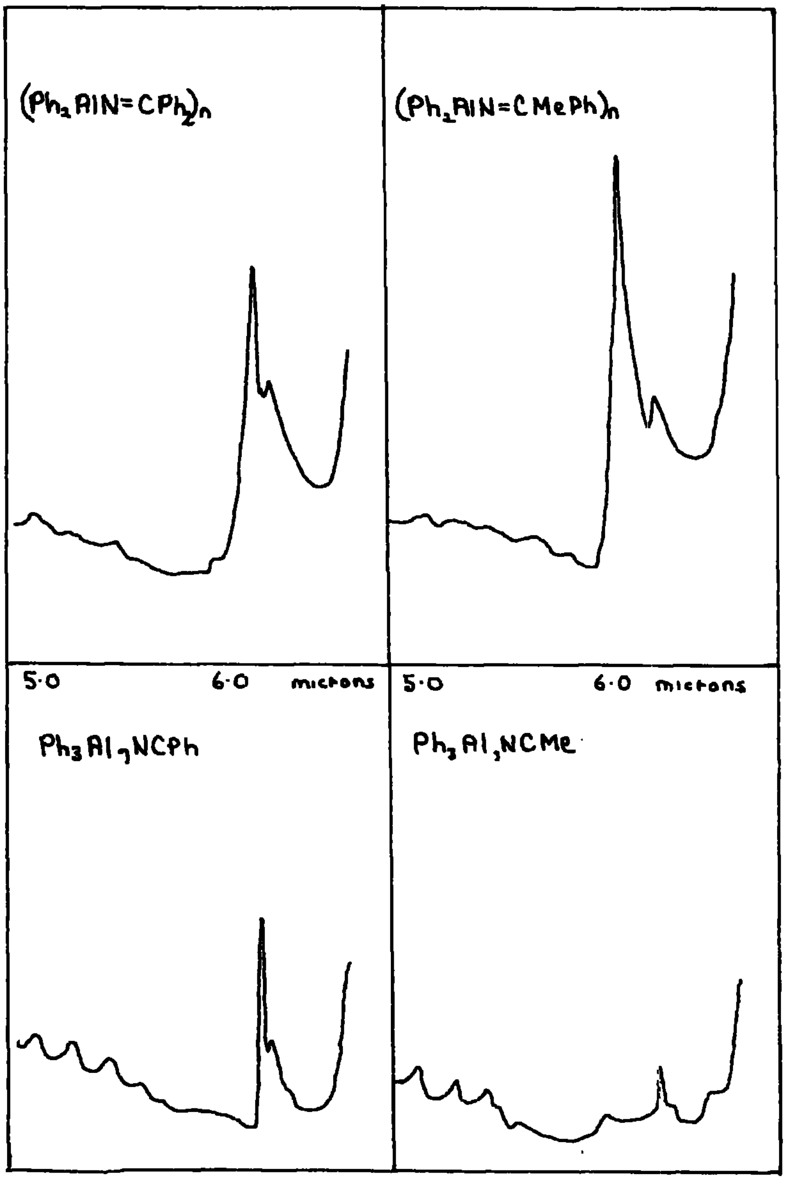
It has been suggested by Gibson and Hughes[89] that the C=N stretching frequency in $(Ph_2AlN{=}CPh_2)_n$ occurs as a small inflexion at 1660 cm.$^{-1}$ However, comparison of the spectra of the compounds above suggests that it is more likely to be the strong band at 1595 cm,$^{-1}$ see Fig. 2 .

The aluminium-nitrogen stretching frequency has been assigned in mono- and bis-trimethylamine-alane at 553 and 460 cm.$^{-1}$ respectively.[103] In most of the compounds prepared a weak broad band occurs between 443 and 471 cm.$^{-1}$ which is assigned, as is shown in Table 5 , to this Al-N stretching vibration.

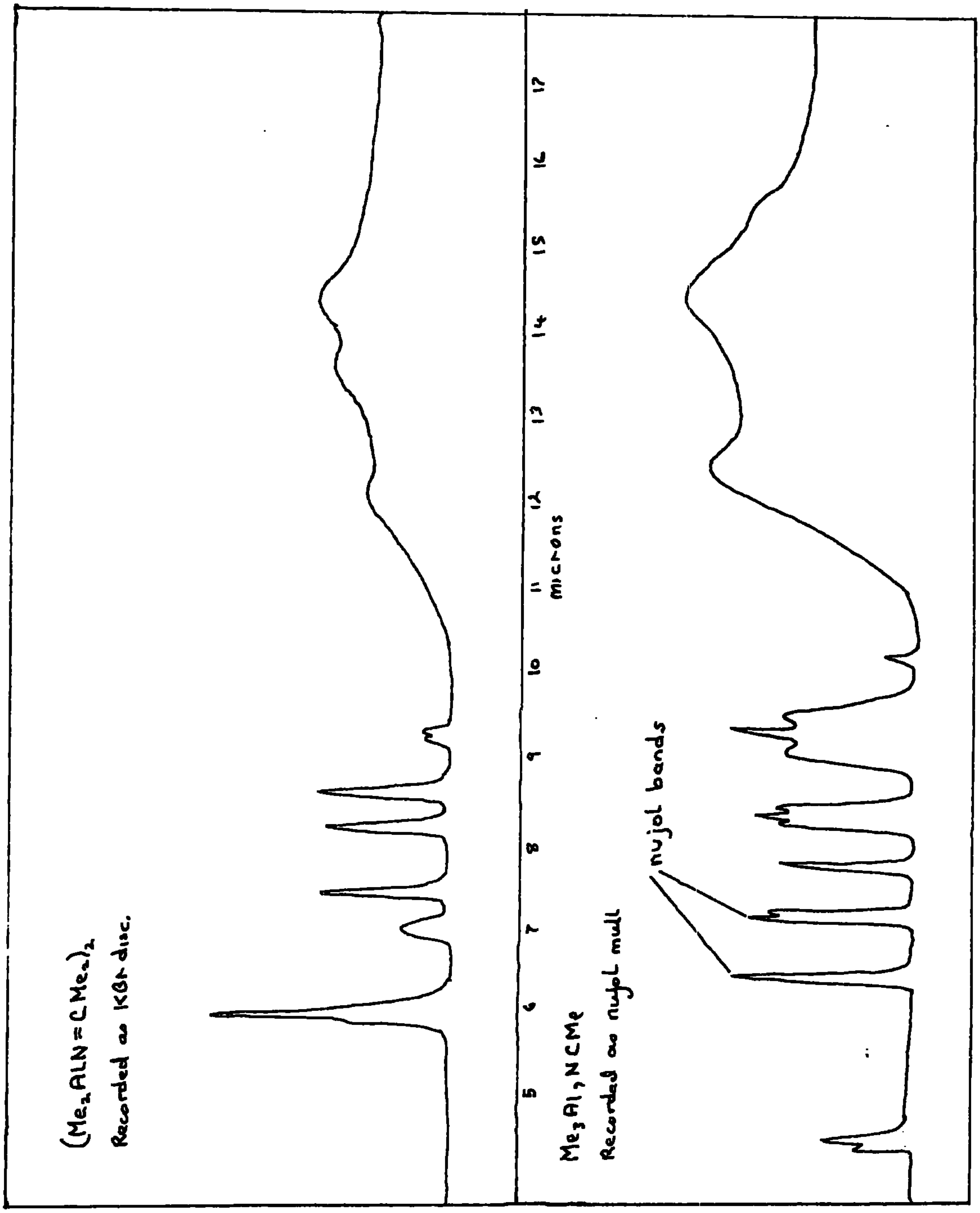
Bands due to the aluminium-methyl stretching frequencies in trimethylaluminium and related compounds were assigned by Hoffmann[104] at 680 cm.$^{-1}$ and those due to aluminium methyl deformation modes at 1200 cm.$^{-1}$

The C=N region of the infrared spectra of the compounds prepared from triphenylaluminium

Figure 2



The infrared spectra of $(Me_2AlN{=}CMe_2)_2$ and $Me_3Al,NCMe$.



A more recent report on the spectra of these compounds[106] (i.e. Me_3Al, Me_2AlCl and $MeAlCl_2$) gives the Al-methyl rocking modes as being at 720 $cm.^{-1}$ which is close to the assigned Al-methyl stretching vibration. This has been substantiated by a study of a variety of aluminium-methyl compounds of the type $(Me_2AlDR_2)_n$ where D = P, As, N done in this laboratory.[105]

From the list of compounds in Table 2a, p.128 in the experimental section it can be seen that bands occur in all the spectra in these regions, so that using this information most of the bands in the simplest spectrum, that of $(Me_2AlN{=}CMe_2)_2$, have been assigned as follows:

The spectrum of isopropylideneaminodimethylaluminium dimer

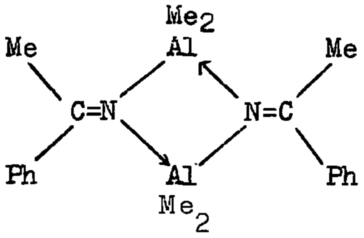
(recorded as KBr disc and nujol mull)

$(Me_2AlN{=}CMe_2)_2$ $cm.^{-1}$	Assignments
3330 vw	C=N (stretch, overtone)
2990 w	C-H (stretch)
2920 ms	C-H (")
2880 w	C-H (")
1715 sh 1656 s	C=N (")
1433 mbr	$C(Me_2)$ (δ)

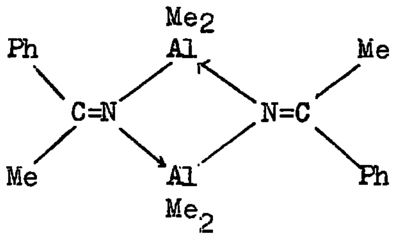
$(Me_2AlN{=}CMe_2)_2$ cm.$^{-1}$	Assignments
1366 ms	$C(Me_2)$ (δ)
1235 ms	
1181 ms	Al-Me (d) sym.
1087 w	C-C (stretch)
1075 w	C-C
833 mbr	$C(Me)_2$
722 msbr	Al-Me (rock)
684 sbr	$AlMe_2$ (stretch)$_{asym}$
553 wbr	AlMe (stretch)$_{sym}$
465 mbr	Al-N (stretch)

Stereochemistry

In several of the alkylideneamino derivatives prepared there was a possibility of isomerism. Firstly, by two different arrangements of the alkylidene group, as in the boron compounds already discussed, e.g.

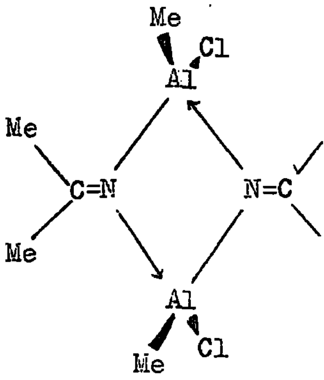


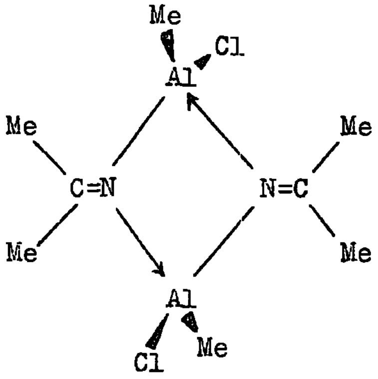
IIIa



IIIb

and also in the compounds derived from Me_2AlCl, by two arrangements on the aluminium atoms; e.g. in $(MeClAlN{=}CMe_2)_2$ where two isomers were possible, and in $(ClMeAlN{=}CMePh)_2$ where four isomers were possible, e.g.





None of these compounds was resolved into isomers, but by analogy to the boron compounds it was expected that the proton n.m.r. spectra of the mixtures would show the existence of isomers if they were present.

Nuclear magnetic resonance spectra

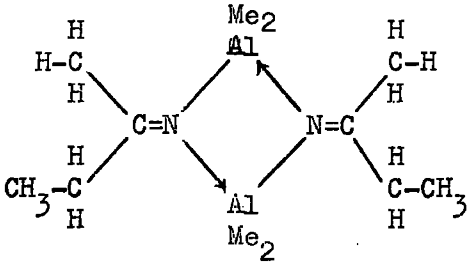
The spectra were recorded on solutions of the compounds in carbon tetrachloride or benzene with tetramethylsilane as internal reference. It was not possible to record spectra on all of the compounds since some were insoluble. A summary of the spectra follows in Table 6 .p76.

It was possible to interpret some of the spectra fully.

1. $(Me_2C{=}NAlMe_2)_2$. This compound showed two peaks of equal intensity; one at + 56 c/s to high field of tetramethylsilane and one at -126 c/s. On the basis of the results on the boron compounds and on the work[107] on Me_2AlCl the peak at + 56 c/s is attributable to the Al-methyl groups and the peak at -126 c/s to the C-methyl groups. Only one isomer of this compound is possible so that the peaks were single and well defined.

2. $(MeEtC{=}NAlMe_2)_2$. Two isomers of this compound are possible, but no evidence of these was obtained in the n.m.r. spectrum. The singlet at + 56 c/s is attributable to the Al-methyl groups and the singlet at -126 c/s to the C-methyl group. The quartet at -140 c/s arises from the $-CH_2-$ group of the ethyl group, and the triplet at -76 c/s from the CH_3 group being split by the $-CH_2-$ group.

The absence of splitting in the peak due to the Al-methyl groups does not necessarily mean that only one isomer was present since the orientation of the ethyl groups may be as follows,



when each $Al(Me)_2$ group may be closest to two $-CH_2-$ groups.

3. $\underline{(MeHC{=}NAlMe_2)_n}$. This compound, which is analogous to $(MeHC{=}NBMe_2)_2$, had peaks in the places expected for hydrogen of =CMe-H (-506 c/s), for the C-methyl (-130 c/s) and Al-methyl (+53 c/s). But all these peaks were complex and it was impossible to interpret them fully. The main features are consistent with the presence of the two expected isomers and the extra peaks of lower intensity may be due to reaction with the solvent.

4. $\underline{(MePhC{=}NAlMe_2)_2}$. Again two isomers are possible and the n.m.r. spectrum shows them to be present. The three peaks to high field do not form a triplet and are best explained as a singlet at + 56 c/s from the four equivalent Al-methyl groups in a <u>trans</u> structure, IIIb p.71 and two smaller peaks of equal intensity at + 39.8 and + 69.5 from the two non-equivalent sets of Al-methyl groups in a <u>cis</u> structure IIIa p.71 (since one set have two methyl groups as nearest neighbours and the other set have two phenyl groups). The phenyl

group gives rise to a broad peak at -446 c/s and the C-methyl groups to two peaks at -136 c/s. These two C-methyl peaks are probably due to two slightly different chemical shifts in the two isomers.

5. $(PhHC=NAlMe_2)_2$. No evidence was obtained for isomeric forms. The compound was not very soluble so that the peaks are rather weak. A singlet at + 426 c/s is attributable to the Al-methyl groups and at - 452 c/s to the phenyl groups. The hydrogen peak was not visible, but would be expected near the phenyl peak.

6. $(PhHC=NAlEt_2)_2$. A single peak at - 440 c/s is due to the phenyl group. A poorly defined quartet at - 60 c/s arises from the CH_2 of the ethyl groups and a poorly defined triplet at 0 c/s arises from the CH_3 groups. The complexity of the spectrum, because of the ethyl groups on the aluminium, makes interpretation in terms of isomers impossible (cf. $(MeHC=NBEt_2)_2$).

7. The spectra of $MeCN,AlMe_2Al$ and $(Me_2C=NAlMeCl)_2$ (liquid form) were obtained in benzene solution. The former had two peaks; the one to higher field (+ 8.7 c/s) due to the Al-methyl groups and the other, of half the intensity, due to the C-methyl groups (- 45 c/s). The spectrum of the liquid $(Me_2C=NAlMeCl)_2$ obtained from the thermal decomposition of this adduct had peaks at similar chemical shifts but they were complex. A weak peak at

- 15 c/s is of uncertain origin. Isomerism as a result of different orientation of the (AlMeCl) groups would not be expected to give rise to different peaks in the spectrum.

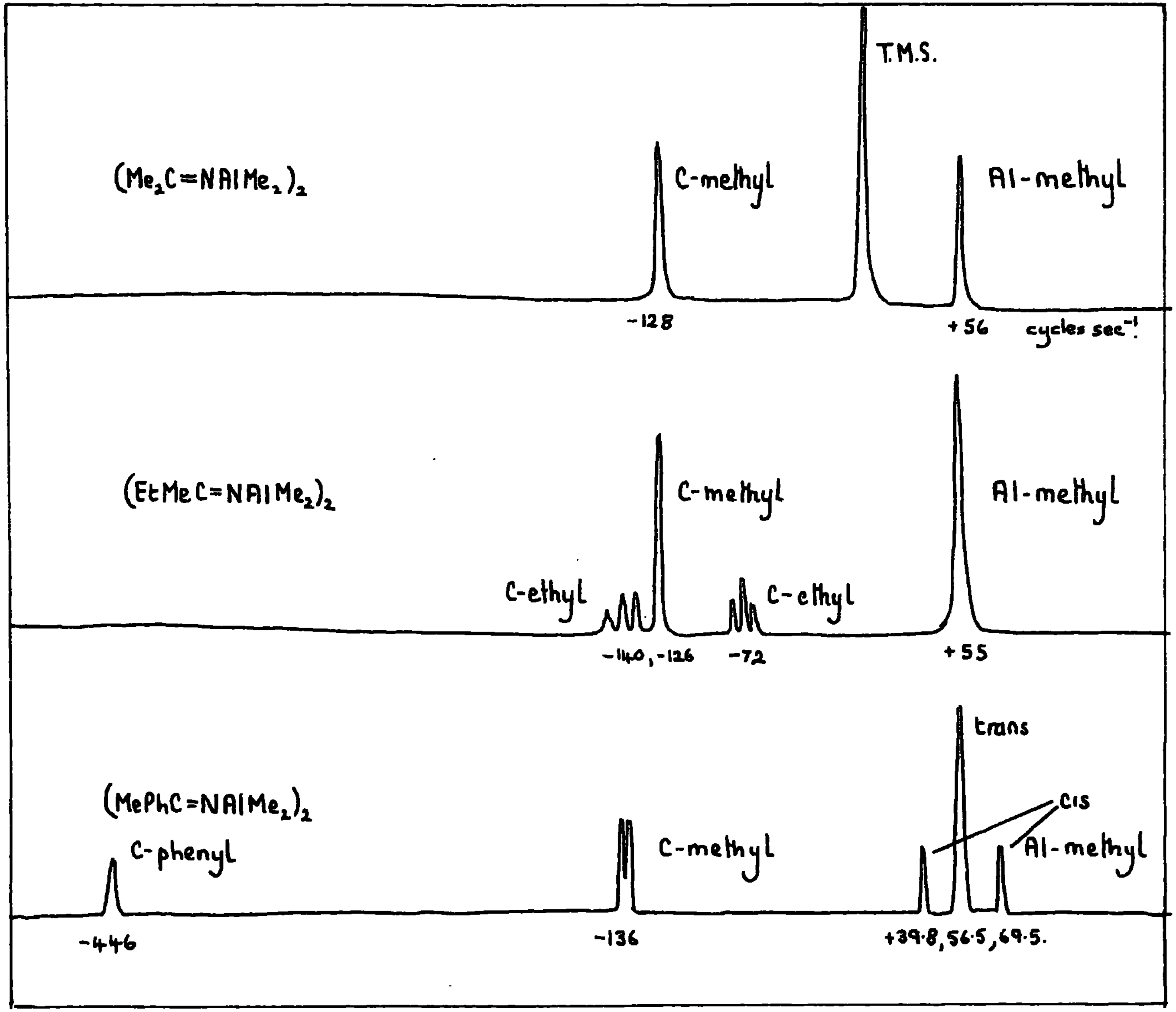
Table 6.

The proton n.m.r. spectra of the rearranged compounds

Solvent, carbon tetrachloride; reference tetramethylsilane; relative intensities in parenthesis.

q = quartet; t = triplet; d = doublet; s = singlet; c = complex.

Compound			Peaks, in cycles. seconds^{-1}		
	=C-H	=C-Ph	=C-Et	=C-Me	Al-Methyl
$(Me_2C{=}NAlMe_2)_2$				-126s(1)	+ 56 (1)
$(MeEtC{=}NAlMe_2)_2$			-140q, J=7.3; -72t, J=7.7; (5)	-126s(3)	+ 55 (6)
$(MeHC{=}NAlMe_2)_2$	-506c(1)			-130c(3)	+ 53c(6)
$(MePhC{=}NAlMe_2)_2$		-446s		-136d,J=3.5	+ 39.8, 56.5,69.5
$(PhHC{=}NAlMe_2)_2$		-452s			+ 42.6
$(PhHC{=}NAlEt_2)_2$ (approx.values)		-440s		Al-Et -60q 0t	
Solvent benzene; reference tetramethylsilane.					
MeCN, $AlMe_2Cl$				-45s(1)	+ 8.7s (2)
$(Me_2C{=}NAlMeCl)_2$ liq				-82s, -15d, J=3;	+ 22s



The proton nuclear magnetic resonance spectra of some organo-aluminium compounds.

Mechanism of the reactions of organo- and hydrido- compounds of boron and aluminium with nitriles

Reactions between dialkylboranes R_2BH and nitriles R'CN proceed normally to the stage $(R'CH{:}N.BR_2)_n$. There is at present no evidence that further reaction with R_2BH leads to diborylamines. The present work suggests that such reactions as,

$$(MeCH{:}N.BMe_2)_2 + (Me_2BH)_2 \longrightarrow 2EtN(BMe_2)_2$$

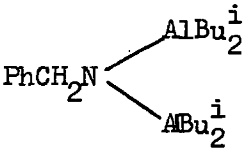
are unlikely because of the comparatively low reactivity of the dimeric ethylideneaminodialkylboranes, in which the boron and nitrogen atoms are co-ordinatively saturated. In systems where the groups R attached to the boron are so bulky as to preclude dimerisation, as may be the case in the intermediates involved in the reactions between nitriles and disiamylborane, further reaction may be prevented for steric reasons:[108]

$$(\text{i-amyl})_2BH + R'CN \longrightarrow R'CH{:}NB(\text{i-amyl})_2$$

$$\xrightarrow[\times]{(\text{iso-amyl})_2BH} R'CH{:}N\,[B(\text{i-amyl})_2]_2$$

In the case of aluminium Ziegler reported that 2 mols. of tri-isobutylaluminium reacted with phenyl cyanide to give 2 mols. butene and a product affording $PhCH_2NH_2$ on hydrolysis.[63] However, Zakharkin[62] found that 1 mol. of di-isobutylaluminium hydride reacts at similar temperatures with PhCN to give $(PhHC{=}NAlBu^i_2)_n$ which suggests that in the former reaction two $Bu_2{}^iAl$ groups are attached to the nitrogen atom rather than that an intermediate $(PhHC{=}NAlBu^i_2)_n$ rearranged further to $(PhCH_2NAlBu^i)_m$

i.e.

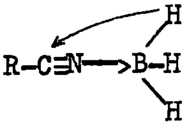


$PhCH_2N(AlBu^i_2)_2$

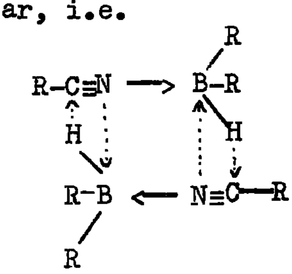
may be formed.

If this deduction is correct, and the intermediate $(PhHC{=}NAlBu^i_2)_n$ does in fact react with Bu_3Al to form $PhCH_2N(AlBu_2)_2$, this would be consistent with the greater reactivity of the aluminium intermediates $(RCH{=}NAlR'_2)_n$ as compared with their boron analogues.

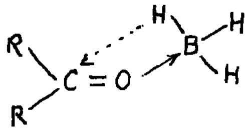
The actual mechanism of transfer of the groups to the carbon atom is unknown but it seems that it is more likely to be intermolecular than intra-molecular, i.e.



unlikely



This may well be different from the case of the carbonyls where the hydrogen atoms are more favourably placed for intramolecular rearrangement:



Similar mechanisms may be proposed for the aluminium compounds.

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Experimental

Experimental methods and apparatus

Nitrogen supply

The nitrogen used was purified by passing the gas through a copper furnace at *ca.* 400°C. and then through molecular sieve (type 5A) since most of the more air sensitive compounds reacted vigorously with nitrogen straight from the cylinder. Periodically the copper was regenerated with hydrogen and the molecular sieve dried by pumping at 300°C. The nitrogen, even when it had been treated like this, was sometimes still moist and was improved considerably by passage through a trap cooled by liquid air or nitrogen.

Glove box

In many cases involatile samples for analysis and infrared spectra were made up under nitrogen in a glove box of the conventional type. The nitrogen used was passed through a recycling system as for the supply described above. A triisobutylaluminium bubbler was found to give drier nitrogen and in conjunction with a liquid air trap made the box extremely good for the most sensitive compounds. It was difficult to prevent some aluminium oxide smoke from entering the box although the gas was passed through a trap filled with glass wool.

Vacuum system[1]

A vacuum system was built for the manipulation of many of the compounds. Its construction involved the use of both mercury float valves and greased taps for storage, fractionation and gas analysis. The storage section had large (2,3 or 5 litre) bulbs so that gases, e.g. trimethylborane or diborane, could be stored. These were closed by mercury float valves or mercury sealed taps.

The section used for fractionation consisted of four U-traps connected by greased T-taps. The use of these taps sometimes allowed the traps to be cleaned without being cut off.

A measuring bulb section consisted of a large bulb and cold finger (4010 c.c.) connected by a mercury float valve to a smaller bulb and cold finger (437.5 c.c.). A single limb manometer was connected to the smaller section so that either a small amount of gas could be measured in the small section alone or a larger amount in the combined sections.

The bulbs were calibrated by condensing in known amounts of carbon dioxide. They were used to measure condensible gases and the bulk of partly condensible ones, e.g. methane.

The rest of the partly condensible gas could be measured in the Töpler pump which was fitted next in the line. This used a mercury pump involving a secondary low vacuum system and the gas was collected in a gas burette. Pressures were measured relative to a manometer beside the gas burette. There was also a section for the measurement of vapour pressures above room temperature. Samples were condensed into a bulb of known volume (ca. 150 c.c.) which could be closed by a mercury U-tube acting also as a manometer. The whole apparatus was immersed in a five litre bath of oil which was heated by an electric immersion heater connected to an auto-transformer.

Several inlet points were fitted using B14 and B10 sockets. A rotary oil pump with a mercury diffusion pump was used for evacuation and a water pump for the low vacuum line.

Calibrations for the measuring system

Combined volume of large and small bulbs = 4455.5 c.c.

Small bulb (to the scratch mark) = 437.5 c.c.

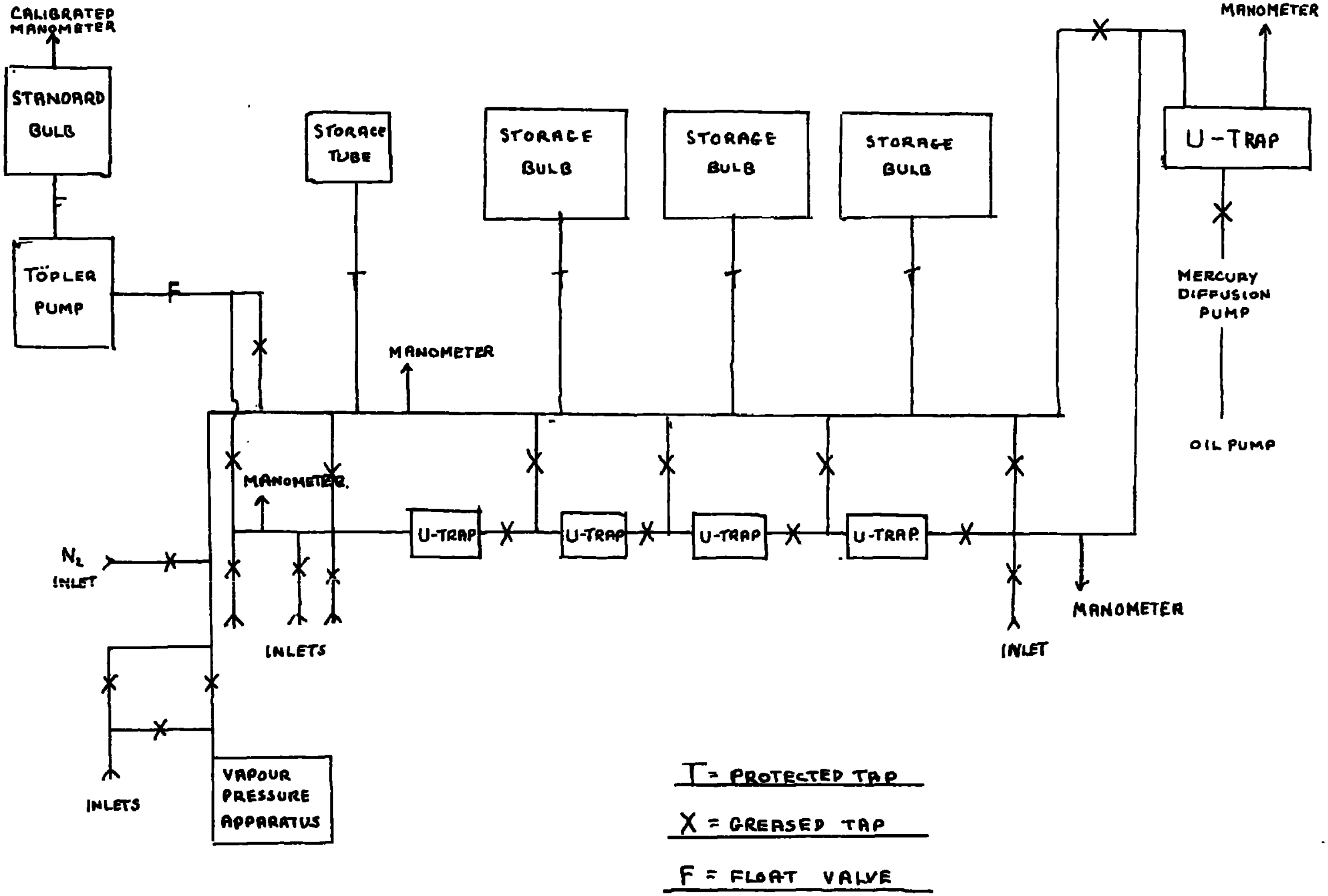
Therefore large bulb = 4018 c.c.

Internal radius of the manometer = 0.427 cm.

Apparent internal radius of the reservoir = 1.875 cm.

For a 1 cm. drop on the manometer the increase in volume = 0.572 c.c.

For a 1 cm. drop on the manometer the rise in the reservoir = 0.0519 cm.



Schematic Diagram of the Vacuum System

Molecular Weight measurements

Molecular weights were determined where possible cryoscopically in benzene. The benzene, of analytical reagent purity, was dried over sodium wire; each bottle being calibrated with biphenyl. The usual Beckmann apparatus was used and since most of the compounds were air sensitive a current of dry nitrogen was passed through the system throughout each determination.

A few measurements were carried out in the vapour phase above room temperature using the apparatus described in the section on the vacuum system. This involved either condensing into the standard bulb weighed volatile samples, or placing in the bulb, through a hole blown in the side, a weighed sample in a small open tube. After the sample was thus introduced the hole in the glass bulb was closed carefully so that the total volume was altered by only a negligible amount. The pressure was measured with the manometer when all the material was in the gas phase and the bath temperature taken with an accurate mercury thermometer. Corrections were made for the changing density and vapour pressure of the mercury in the manometer which became significant above 100°C.

Infrared Spectra

Infrared spectra were recorded on a Grubb-Parsons' GS2A prism-grating spectrometer, (range 2 to 25 microns), or Spectromaster.

Spectra of solid compounds were recorded using either pressed KBr discs, or nujol (liquid paraffin) mulls between two KBr discs, or occasionally using solutions in carbon tetrachloride. The spectra of liquids were recorded using KBr liquid cells. Gaseous spectra were all recorded using 10 cm. sodium chloride cells.

In the case of one solid the spectrum was obtained in a Perkin-Elmer heated gas cell. The solid was introduced through a plug in the side, the plug was replaced and the cell quickly pumped out and the valve closed. The cell was then heated electrically, temperatures being recorded on a thermocouple recorder.

When measurements were needed above 21 microns the recording speed was reduced (motor speed 4 r.p.m. to 1 r.p.m.) otherwise weaker peaks did not appear.

Nuclear Magnetic Resonance Spectra

These were recorded on an A.E.I. R.S.2 spectrometer operating at 60 Mc/s. Samples were dissolved in carbon tetrachloride with tetramethylsilane as the reference compound. In some cases the compounds were condensed into the sample tubes under vacuum which avoided contact with air; otherwise the solutions in carbon tetrachloride were made under nitrogen and transferred to the tubes by syringe.

Analytical Methods

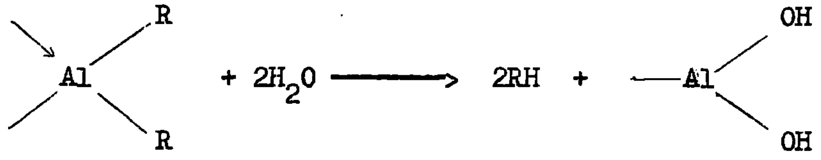
Carbon and Hydrogen analysis

In many cases the compounds were too air sensitive for carbon and hydrogen analysis to be carried out satisfactorily. Analyses for these elements which were carried out were done either in the department by Mr. T. Cagill or by external professional analysts.

Hydrolyses:

The air sensitive compounds were mainly attacked by moisture and the gas given off easily measured.

e.g.



where R = H, Me or Et.

In the case of R being phenyl the compound was allowed to react over about an hour at room temperature with dry hydrogen chloride. The benzene produced was condensed into a small flask and weighed.

If possible, volatile samples were condensed into a flask, weighed, and then transferred on the vacuum line to another flask in which they were hydrolysed. In some cases solids were transferred to a small two-necked flask under nitrogen using ungreased joints; in other cases the materials were transferred in the glove box, in particular involatile liquids which had to be moved by syringe. The flask was then attached to the vacuum system and a dropping funnel fitted into the other neck. The compounds were hydrolysed with a few c.c. of de-aerated 2-methoxyethanol followed by dilute sulphuric acid. The gases liberated which did not condense in liquid nitrogen were measured in the gas burette using the Töpler pump.

Aluminium Analysis

The solution from the hydrolysis obtained as described above was analysed for aluminium by either the oxine or the EDTA method.

Oxine Method[2]

A sample containing about 0.02 g. aluminium was boiled to near dryness with addition of a little conc. nitric acid. The white solid left was dissolved in a minimum amount of dilute hydrochloric acid and diluted to 150 c.c. The pH of the solution was then about 6. After warming to 50-60°C. a 20% excess of a 2% solution of 8,hydroxyquinoline in acetic acid was added, followed by 40 g. of ammonium acetate dissolved in the minimum amount of water. The precipitate was allowed to settle and was then collected in a weighed sintered glass crucible, washed with hot water and dried at 110°C.

EDTA Method[3]

The whole of the solution left after hydrolysing a sample containing about 0.020 g. of aluminium was placed in a large conical flask. The flask containing 2,methoxyethanol together with any other organic matter was heated until the contents boiled in order to get rid of volatile materials. If, after the flask was almost dry, organic material remained this was destroyed with small amounts of concentrated nitric acid. After this treatment a white solid was left when the flask was at near dryness. This solid was dissolved in a minimum amount of dilute sulphuric acid, cooled and the solution made up to 100 ml.

A 10 ml. aliquot of this was taken and titrated with standard caustic soda, usually about 0.2N, with B.D.H. 4.5 indicator, the end point being when this just turned blue. A further 10 ml. aliquot was taken and about 0.1 ml. less than the amount noted of the caustic soda solution added without the B.D.H. indicator. Then 10 ml., an excess, of 0.01M. EDTA solution was added, a drop of xylenol orange solution and a few crystals of hexamine. The solution was warmed slightly and titrated with 0.01M. zinc acetate solution. A sharp change from yellow to red indicated the end point.

Sometimes a bad end point occurred; either a slow change of colour or the solution turned brown, or no end point at all. This was usually due to the pH of the solution being wrong, e.g. too much hexamine. Other causes have been that all of the organic material, especially amines, was not destroyed or, in one case, bad demineralised water. The indicator, xylenol orange, must also be made up freshly at frequent intervals. Finally, the solutions and the hexamine must be added in the right order.

Reagents

0.01M. EDTA and zinc acetate solutions.

0.2-0.5 caustic soda solution. 0.2-1% aqueous xylenol orange.

B.D.H. 4.5 indicator and solid hexamethylenetetramine.

Boron Analyses[4]

These were done by two methods.

Method 1 (Methyl borate method)

A quantity of the compound (0.1-0.2 g.) was destroyed in 50 c.c. hot concentrated sulphuric acid in a flask fitted with a dropping funnel and a condenser. To this 25 c.c. dry methanol were added slowly, drop by drop. The solution became very hot and it was ensured that each drop of methanol mixed with the acid by shaking, otherwise the solution would suddenly boil vigorously out of the condenser. The solution was then gently refluxed for 30 minutes and cooled. The flask was fitted with a distillation head and the methyl borate formed in the process distilled out with about 10-15 c.c. methanol into a flask containing 25 c.c. water. This solution, after adding ca.3 g. mannitol, was titrated with standard caustic soda.

The second method is quicker than this one, which has the drawback that very dry methanol is needed. This was dried by refluxing it with magnesium methoxide and distilling it off. The apparatus must also be carefully put together so that none of the volatile trimethyl borate is lost.

Method 2[5] (Combustion method)

The apparatus used was as 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 either in the glove box or in the air. The amount used was up to 0.10 g. The large dropping funnel was purged with oxygen and 25 to 50 c.c. water placed in it. The gelatine capsule was placed in the platinum gauze with a small piece of filter paper to act as a fuse. This was lit and quickly placed in the flask. After a few seconds the compound burned with a bright green flame. When the combustion was complete the flask was shaken to dissolve the combustion products. The contents were then rinsed into a flask made up to a standard volume and titrated with caustic soda in the presence of mannitol. The indicator was bromothymol blue.

Nitrogen Analysis

This was done by the normal Kjeldahl method. The sample was destroyed in concentrated sulphuric acid, sometimes the solution from the boron analysis being used. This was then transferred to a small Kjeldahl flask, made alkaline with strong caustic soda and boiled. The amine was steam-distilled into a flask containing a known amount of standard acid. After twenty minutes' distillation the remaining acid was titrated with standard alkali.

Preparation of the starting materials

Trimethylborane b.p. -21.8°C.

This was prepared by the Grignard method. Methyl magnesium bromide was prepared in dibutyl ether, dibutyl ether being used to facilitate the purification of the product.

$$3MeMgBr + Bu_2O,BF_3 = Me_3B + Bu_2O + 3MgBrF$$

Two traps were then connected to the condenser and flushed out with nitrogen, which was left flowing as a slow stream for the rest of the experiment. The first trap was cooled by an acetone bath in a vacuum flask cooled to -78°C. by solid carbon dioxide, and the second by liquid air. Boron trifluoride-dibutyl ether complex was then added to the Grignard reagent and the flask warmed to 70°C. to complete the reaction. Nearly all the borane collected in the liquid air trap; further purification was carried out in the vacuum line using a methylene chloride slush bath to trap out any impurity, mainly dibutyl ether. The purity of the final product was checked by vapour density measurements and its infrared spectrum.[6] (Yield: 90-95%).

Further samples were prepared using trimethyl borate instead of boron trifluoride but the yields were not as good, (ca.60%).

Triethylborane b.p. 95°C.

This was prepared similarly to trimethylborane.

$$3EtMgBr + Et_2O,BF_3 = Et_3B + Et_2O + 3MgBrF$$

The Grignard reagent, ethyl magnesium bromide, was used in diethyl ether since the product, a liquid boiling ca. 95°C. is easily separable from it. The purity of the product was checked after fractionation in the vacuum line by vapour density measurements and its infrared spectrum.[7]

Diborane[8]

Twice the amount of boron trifluoride-ether complex calculated from the equation was added to a solution of sodium borohydride in diglyme contained in a three-necked flask.

$$3NaBH_4 + 4Et_2O,BF_3 = 2B_2H_6 + 3NaBF_4 + 4Et_2O$$

To the flask were fitted a mercury sealed stirrer, a dropping funnel and a water condenser. The outlet of the condenser was connected to two traps both cooled in baths of liquid air. The whole apparatus was flushed out with nitrogen before use and a slow stream was allowed to pass through the apparatus during the whole experiment. After the boron trifluoride-ether complex had all been added the flask was warmed slowly to complete the reaction. The traps were then closed and quickly connected to the vacuum line where the diborane was fractionated and stored in a three-litre bulb. (Unless the material is used in situ, ample storage space for the gas must be provided). The purity was checked by vapour density measurements and by its infrared spectrum.[9] Very good yields are obtainable, (ca. 95%).

1,1 Dimethyldiborane

This was prepared by allowing equimolar quantities of diborane and trimethylborane to equilibrate in the gas phase at room temperature.[10]

$$2Me_3B + 2B_2H_6 = 3Me_2BH.BH_3$$

The gases were measured in the standard bulb and then placed in a larger bulb for a few days, after which infrared spectra and gas density measurements were taken. The average molecular weight of the product was then 56 as required for dimethyldiborane, $Me_2B_2H_4$, compared to an average molecular weight of 42 if the diborane (M.28) and the trimethylborane (M.56) were unreacted. The infrared spectrum showed bands corresponding to those found for 1,1 dimethyldiborane by Shapiro and his co-workers.[11] Extra bands revealed the presence of some mono- and trimethyldiboranes but these compounds were not separated as their equilibrium concentration would have been regenerated under the conditions under which it was to be used.

Typical amounts of materials used are recorded in the reports of individual reactions.

Tetramethyldiborane

This was prepared similarly to the 1,1 dimethyldiborane above.[10]

Diborane (1 volume) was allowed to equilibrate with trimethylborane (5 volumes).

$$4Me_3B + B_2H_6 = 3Me_2BH.BHMe_2$$

The slight excess of trimethylborane over the theoretical amount was to avoid the formation of dimethyldiborane. The equilibrium mixture contained some trimethyldiborane and unchanged trimethylborane which could be detected by bands in the infrared spectrum[12] at 2510, 1300 and 1150 cm.$^{-1}$ The material was used without fractionation because again the conditions under which it was allowed to react would have regenerated the equilibrium mixture, particularly dimethyldiborane which it was necessary to avoid.

1,1 Diethyldiborane

This was prepared by the action of vinyl bromide on sodium borohydride.[13]

$$2CH_2{=}CHBr + 2NaBH_4 = Et_2BHBH_3 + 2NaBr$$

It was found that the most suitable solvent was tetraglyme which is easily separable from the product. The gases evolved were passed through a trap cooled by a methylene chloride slush bath (-96°C) and then through a trap cooled in liquid air. It was found from vapour density measurements that the 1,1 diethyldiborane was in the trap cooled in the slush bath and that a little diborane was in the liquid air trap. The compound was further fractionated in the vacuum line through a methylene chloride slush bath and then the vapour pressure was 4 cm. at 0°C. The infrared spectrum was recorded and compared with that of Shapiro and his co-workers.[12]

Tetraethyldiborane

Diborane (1 volume) was mixed with triethylborane (5 volumes) in a bulb of three litres in volume and allowed to stand for two weeks, (see individual experiment).

Trimethylaluminium m.p. 15.0°C., b.p. 126°C.

This was technical grade material as supplied by Ethyl Corporation. The cylinders, each containing $^1/2$ lb. of material were emptied into two-necked flasks using teflon taps and teflon sleeves on the joints.[14] It was purified by distillation under vacuum and was generally distilled into the reaction vessel. The material was also moved by syringe which is easy and safe if all the apparatus and the syringe are flushed with nitrogen.

Triethylaluminium m.p. -52.5°C., b.p. 185.6°C.

Commercial material was again available in cylinders and was removed and stored as with trimethylaluminium. Some was purified by distillation under reduced pressure but in several cases the material was used for the reactions straight from the cylinder and the products purified by distillation.

Triphenylaluminium m.p. 225-228°C.

The triphenylaluminium ether complex (m.p. 127-128°C.) was prepared from phenyl lithium and aluminium chloride in ether.[15]

$3PhLi + AlCl_3OEt_2 = Ph_3AlOEt_2 + 3LiCl$

The complex was purified by recrystallisation from toluene. The ether can be recovered from the complex at 160-170°C. but this was not done with the sample used in the following reactions.

Dimethylaluminium hydride

This was prepared by M. Tranah in connection with other work in the laboratory. The method used was the reaction between trimethylaluminium and lithium aluminium hydride in methylcyclohexane in a sealed tube at 70°. After 24 hours the tube was cooled and the contents distilled out under vacuum.

$$LiAlH_4 + AlMe_3 = Me_2AlH + LiAlH_3Me$$

The material was conveniently used as a solution in methylcyclohexane, since the pure hydride is a highly reactive viscous liquid.

Dimethylaluminium chloride

This was prepared by distillation of methyl aluminium sesquihalide to which sodium chloride had been added. Only the monohalide distills out of this mixture since the sodium chloride complexes with the dihalide forming an involatile compound:

$$NaCl + Me_3Al_2Cl_3 \longrightarrow NaAlMeCl_3 + Me_2AlCl$$

Experimental Results

Boron Compounds

Reaction of methyl cyanide with trimethylborane

Methyl cyanide and trimethylborane were recovered unchanged from mixtures of these compounds. Gaseous trimethylborane was left for two weeks at room temperature with liquid methyl cyanide and for about an hour at 60°C. with refluxing methyl cyanide. No sign of interaction was observed in the infrared spectrum of the gaseous mixture, or in the vapour density, or in vapour pressure measurements at low temperatures.

Reaction of methyl cyanide with triethylborane

Triethylborane (0.1836 g., 0.19 m.mole) and methyl cyanide (0.0678 g., 0.17 m.mole) were sealed in a bulb of volume 100 c.c. This was placed in a water bath at 100°C. over a day when no noticeable reaction occurred. The flask was then placed in an oven and the temperature was increased to 300°C. for half an hour. On opening the flask a small amount of ethylene was found to be present (2 c.c.), but essentially the reactants were unchanged. Repeating the reaction at 340°C. for several days produced no further results.

Reaction of methyl cyanide with tetramethyldiborane

Trimethylborane (0.956 g., 17.1 m.mole) and diborane (0.0945 g., 3.4 m.mole) were mixed in a bulb of volume 1050 c.c. and left at 20°C. for two days; methyl cyanide (0.789 g., 19.3 m.mole) was then distilled in. At 20°C. most of the methyl cyanide and tetramethyldiborane remained in the liquid phase. Colourless crystals grew on the vessel walls during six days at room temperature. The reaction mixture was then transferred to the vacuum line and separated into unchanged trimethylborane (0.195 g., 3.5 m.mole), tetramethyldiborane (0.301 g., 3.6 m.mole), methyl cyanide (0.040 g., 0.97 m.mole), and a fraction (1.25 g.) which condensed at -25°C. in the vacuum line. Repeated distillation of this last fraction from traps held at -20°C. to -15°C. separated it into two components, a colourless crystalline solid (Fraction 1; 0.9 g.) v.p. 0.6 mm. at 20°C., and a colourless liquid (Fraction 2; 0.35 g.) v.p. 1.8 mm. at 20°C.

Characterisation and reactions of Fraction 1

Fraction 1 was identified as dimeric ethylideneaminodimethylborane, $(MeCH{=}NBMe_2)_2$, m.p. 76°C.

(Found: C, 58.1; H, 12.0; B, 13.0; N, 17.0%; M (cryoscopic in benzene), 166; M (from vapour density), 158. $C_8H_{20}B_2N_2$ requires C, 57.8; H, 12.1; B, 13.1; N, 16.9%; M, 166).

The infrared spectrum of the gas at 53°C. and 72°C. over the range 4000-525 cm.$^{-1}$ contained bands at 3420 vw, 3060 vw, 3010 vw, 2925 vs, 2905 m(sh), 2840 w(sh), 1700 s, 1524 vw, 1443 w, 1393 w, 1366 w, 1299 s, 1147 m, 1120 w-m, 1096 m, 1042 s, 932 w, 848 w, 715 w, 610 w, and 574 w cm.$^{-1}$ The vapour pressure (20-80°C.) was given by $\log_{10}P_{mm} = 8.775 - 2636/T$. Above about 150°C. pressures were not reproducible, increasing slowly, showing that the compound was decomposing. A sample of Fraction 1 (0.134 g.) heated in a sealed bulb at 155°C. for eighteen hours, was converted into an involatile yellow glue (0.09 g.) together with some trimethylborane (0.020 g.), and an unidentified solid, (Fraction 3: 0.016 g., v.p. ca. 13 mm. at 20°C.). The infrared spectrum of Fraction 3 had shown bands at 3660 vw, 3520 vw, 3450 vw, 3425 vw, 2970 m, 2940 m, 2860 w(sh), 1618 m, 1608 m, 1400 s, 1310 s, 1202 w-m, 1189 w-m, 1160 m, 1130 s, 1100 w(sh), 943 m, 735-730 w, and 672 w-m cm.$^{-1}$ In an attempt to identify Fraction 3, the whole fraction (0.016 g.) was condensed onto cold concentrated sulphuric acid and the mixture was shaken at 20°C. for a few minutes. All the material still volatile (0.006 g.) was then removed, and identified by its infrared spectrum as trimethylborane. The sulphuric acid solution was then treated with an excess of concentrated sodium hydroxide solution, but no volatile materials other than water were detected in the vapour pumped from the residue.

Fraction 1 slowly volatilised without decomposition on exposure to air, and at 20°C. was unaffected by water, dilute acids, dilute alkalis or gaseous hydrogen chloride. Heating with concentrated sulphuric acid decomposed Fraction 1, and this reaction was used in analysing for nitrogen (by the Kjeldahl method) and boron (by the methoxide/mannitol method). Heating with dilute sulphuric acid and passage of the vapours through 2,4-dinitrophenylhydrazine solution yielded acetaldehyde 2,4-dinitrophenylhydrazone.

Reaction of Fraction 1 with an excess of hydrogen chloride gas at 105°C. for two days gave dimethylchloroborane, some trimethylborane and methyldichloroborane, and an involatile amorphous brown solid. Reaction of Fraction 1 with an excess of water vapour at 105°C. for one day gave an involatile yellow solid, dimethylborinic acid, and a trace of methane. Reactions with strong sulphuric acid or sodium hydroxide solutions at 100-150°C. in sealed tubes generated varying quantities of methane and ammonia; no ethylamine was detected among the products.

Characterisation of Fraction 2

Fraction 2 from the reaction of tetramethyldiborane with methyl cyanide proved to be an isomer of Fraction 1, m.p. -5°C.

(Found: C, 56.8; H, 12.3; B, 12.7; N, 16.9%; M (cryoscopic in benzene), 170; M (from vapour density), 159. $C_8H_{20}B_2N_2$ requires

$C_8H_{20}B_2N_2$ requires C, 57.8; H, 12.1; B, 13.1; N, 16.9%; M, 166). The infrared spectrum of the liquid over the range 4000-400 cm.$^{-1}$, showed bands at 3410 vw, 3000 vw, 2920 s, 2900 m(sh), 2825 w (sh), 1740 vw(sh), 1698 vs, 1615 vw, 1433 m, 1401 m, 1362 m, 1289 vs, 1145 ms, 1114 m, 1091 s, 1034 vs, 923 w-m, 844 w, and 824 vw(sh) cm.$^{-1}$ The vapour pressure (20-90°C.) was given by $\log_{10}P$mm = 7.230 - 2044/T. Above about 150°C. pressures increased irreversibly as the compound decomposed, forming an involatile yellow glue, trimethylborane, and traces of unidentified volatile materials similar to those (Fraction 3) found after pyrolysis of Fraction 1. Heating Fraction 2 with water vapour at 100°C. gave dimethylborinic acid and an involatile residue. Heating with dilute sulphuric acid gave acetaldehyde, identified as its 2,4-dinitrophenylhydrazone. Reaction with strong sodium hydroxide solution in sealed tubes at 100-150°C. gave ammonia and traces of methane.

Reaction of methyl cyanide with 1,1-dimethyldiborane

1,1-dimethyldiborane (0.168 g., 3.0 m.mole) and methyl cyanide (0.200 g., 4.9 m.mole) were sealed in a bulb of volume 1050 c.c. At 20°C. some methyl cyanide remained as liquid. During several days at room temperature the liquid became more viscous, the gas pressure in the bulb decreased, and colourless crystals appeared on the bulb walls. After one week the volatile contents of the bulb were transferred to the vacuum line and separated into unchanged 1,1-dimethyldiborane (0.090 g., 1.6 m.mole), unchanged methyl cyanide (0.082 g., 2.0 m.mole), a colourless liquid (Fraction 4; 0.05 g.) v.p. 2.4 mm. at 20°C., and a colourless crystalline solid (Fraction 5; 0.06 g.) v.p. 0.6 mm. at 20°C. Left in the reaction vessel was a viscous colourless liquid (Fraction 6; 0.09 g.) which was involatile at room temperature.

Fraction 4 was identified by its infrared spectrum as N'N''N''' triethylborazine, extra bands indicating the presence of some of the liquid dimeric ethylideneaminodimethylborane, $(MeCH{=}NBMe_2)_2$, described as Fraction 2 above.

Fraction 5 was identified by its infrared spectrum as the solid isomer of dimeric ethylideneaminodimethylborane, $(MeCH{=}NBMe_2)_2$, described as Fraction 1 above.

Fraction 6, the involatile viscous liquid, had an infrared spectrum showing bands at the following frequencies: 3080 m, 2900 m, 2470 m, 2325 m, 1701 m, 1686 w(sh), 1473 m(sh), 1433 s, 1374 m, 1350 m(sh), 1292 m, 1253 m, 1186 w(sh), 1145 m, 1101 m(sh), 1076 m, 1044 w(sh), 962 w, 897 w(sh), 883 m, 793 w, 688 w, and 667 w $cm.^{-1}$ This spectrum was very similar to that of the involatile liquid, product of the reaction between methyl cyanide and diborane, with extra bands which may indicate the presence of methyl groups attached to boron.

Reaction of methyl cyanide with tetraethyldiborane

Diborane (0.178 g., 6.2 m.mole) and triethylborane (3.018 g., 31.5 m.mole) were mixed and left in a bulb of volume three litres for two weeks, and then transferred to a reaction bulb (volume 250 ml.) together with methyl cyanide (1.686 g., 40.6 m.mole). The reaction mixture was mainly liquid at room temperature. After two weeks, the bulb was opened and volatile materials were distilled into the vacuum line and separated into ethane (0.015 g., 0.5 m.mole) and a mixture of methyl cyanide and triethylborane (1.047 g.). Left in the bulb was a colourless liquid (Fraction 7; 3.8 g.), virtually all of which proved just volatile enough at 20°C. to distil slowly in a good vacuum on to a cold finger at -78°C., where it collected as a crystalline solid, melting over the range -18 to -10°C.

Fraction 7 proved to be dimeric ethylideneaminodiethylborane, $(MeCH{=}NBEt_2)_2$.

(Found: C, 65.1; H, 12.7; B, 9.7; N, 12.8% M (cryoscopic in benzene), 221. $C_{12}H_{28}B_2N_2$ requires C, 64.9; H, 12.7; B, 9.7; N, 12.6%; M, 222).

The infrared spectrum of the liquid over the range 4000-400 cm.$^{-1}$, showed bands at 3400 vw, 3000 w(sh), 2940 vw, 2900 vw, 2865 vs, 2820 m, 2715 vw, 1692 vs, 1457 m, 1431 m, 1397 w-m, 1370 w(sh), 1361 w-m, 1272 m, 1256 w(sh), 1227 w(sh), 1144 s, 1098 m, 1082 m(sh), 1056 vs, 1031 w(sh), 1012 vw(sh), 973 vw, 919 s, 903 m(sh), 818 s, 743 vw, and 631 vw cm.$^{-1}$ The vapour pressure (110-180°C.) was given by $\log_{10}P_{mm} = 7.097 - 2,465/T$, which corresponds to a figure of 10 mm. at 131°C., and may be extrapolated to 0.05 mm. at 20°C. Above about 150°C. pressures increased irreversibly as the compound decomposed, forming an involatile viscous liquid, traces of triethylborane, and a trace of a colourless liquid, which had absorption bands in the infrared spectrum at 3580 vw, 3520 w, 3435 w, 2965 vs, 2925 ms, 2890 s, 1616 ms, 1608 ms, 1468 m, 1403 w, 1330 ms, 1242 vw, 1130 m, 1121 m, 1100 m, 1031 w, 966 w, 948 w, 928 w, 835 vw, and 770 cm.$^{-1}$

The diethyl derivative Fraction 7 was unchanged after short exposure to air or moisture, but gave diethylborinic acid when heated with water vapour at 100°C. Heating with dilute sulphuric acid gave acetaldehyde, identified as its 2,4-dinitrophenylhydrazone after passage of the vapours through 2,4-dinitrophenylhydrazine solution. Attempts to separate Fraction 7 into isomers by vapour phase chromatography, using nitrogen as carrier gas over a silicone elastomer at temperatures up to 200°C. were unsuccessful.

Reaction of methyl cyanide with 1,1-diethyldiborane

1,1-diethyldiborane (0.297 g., 3.5 m.mole) and methyl cyanide

(0.142 g., 3.5 m.mole) were sealed in a bulb of volume 1050 c.c. for six days. Easily volatile materials were then pumped into the vacuum line, leaving a colourless liquid. Prolonged pumping on this residual liquid showed some (0.2 g.) to be just volatile enough at 20°C. to be transferred to the line. Its infrared spectrum showed this to be dimeric ethylideneaminodiethylborane, identical with the material Fraction 7 described above. (M (cryoscopic in benzene), 230; $(MeCH{=}NBEt_2)_2$ requires M = 222).

The reaction of boron trifluoride with trans-ethylideneamino-dimethylborane

The solid, trans-ethylideneaminodimethylborane dimer, (0.2142 g., 1.29 m.mole) was placed in a nitrogen-filled flask fitted with a ground glass joint. The neck of the flask was constricted and the nitrogen pumped out on the vacuum line. Boron trifluoride (0.3983 g., 5.85 m.mole) was condensed in, the flask sealed off and allowed to warm to room temperature. No reaction was observed during a few hours and so the flask was placed in an oven at 70°C. just below the melting point of the solid dimer (m.p. 78°C.) for several more hours. As before no reaction was observed and the flask was heated further to 90°C. After one day a slight yellowing appeared on the walls of the flask but on cooling there was a large amount of white solid like the original dimer present. The flask was attached to the vacuum line and opened and the volatile contents pumped out. A gas (0.3775 g.) was removed together with all the other volatile material mainly a white crystalline solid (0.1300 g.). This left a yellow material smeared inside the flask (0.1950 g.). The infrared spectrum of this residue showed the presence of C-F groups but nothing easily identifiable and no ethylideneaminodifluoroborane. The material was insoluble in benzene and ether and no further investigation was carried out.

The white solid which was pumped into the vacuum line was shown to be the starting material, by its vapour pressure and infrared spectrum.

An infrared spectrum of the gas showed bands due to B-Me and B-F vibrations.

Aluminium Compounds

Reactions of trimethylaluminium

Formation of the methyl cyanide adduct, MeCN.AlMe$_3$

Trimethylaluminium (6.40 g., 89 m.mole) and methyl cyanide (3.52 g., 86 m.mole) were condensed in a flask at -196°C., and the mixture was allowed to warm up. The heat evolved in the reaction raised the temperature of the mixture to about 60-70°C. after which a moist solid remained. Unchanged trimethylaluminium (0.210 g., 2.9 m.mole) was pumped off, leaving a colourless crystalline solid, m.p. 73°C., which could be purified by vacuum sublimation at about 70°C.

Found: Al, 23.7; Me, 39.7%; M, 108. $C_5H_{12}AlN$ requires Al, 23.9; Me, 39.8%; M,113.

The infrared spectrum of the solid in nujol or carbon tetrachloride showed bands at 2295 m, and 2315 w cm.$^{-1}$ in the ν(C≡N) region. The adduct was extremely sensitive to air and moisture, slight decomposition occurring even when the compound was transferred in the glove box. (After infrared frequencies the letters correspond to the following terms; s = strong, m = medium, w = weak, (sh) = shoulder, (br) = broad).

Thermal decomposition of the trimethylaluminium-methyl cyanide adduct - formation of isopropylideneaminodimethylaluminium dimer, $(Me_2AlN{=}CMe_2)_2$

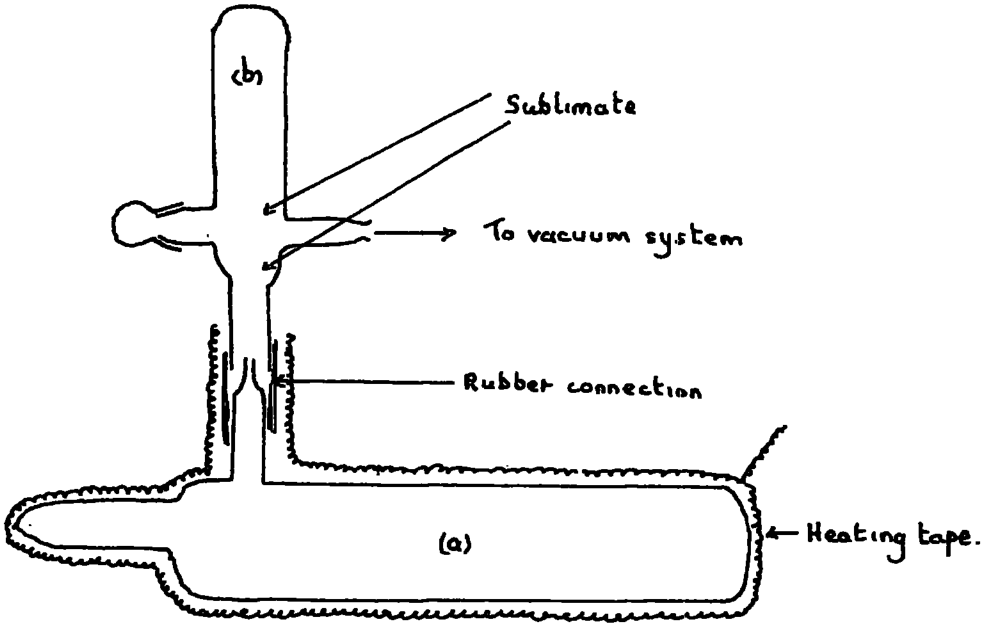
Trimethylaluminium (0.4408 g., 6.12 m.mole) and methyl cyanide (0.2462 g., 6.0 m.mole) were condensed into a tube of volume 180 c.c. fitted with a fragile-tipped side arm. The vessel was sealed under vacuum and heated to 150°C., at which temperature only a colourless liquid was visible. In a few hours the liquid darkened and after five hours solidified to a dark red solid. The tube was then allowed to cool and white crystals condensed on the sides of the tube. The side tube was sealed to the vacuum system with picein wax, and after the fragile tip had been broken the volatile reaction product was transferred to the vacuum system. This was identified by its vapour pressure (1.4 mm. at -196°C.) and its infrared spectrum as methane (80 n-c.c., 3.6 m.mole).

The reaction tube (a) was then filled with nitrogen and connected by a short piece of rubber tubing to a second tube (b) as shown in Fig. 1a. The apparatus was once more evacuated and tube (a) was heated to about 100°C. with heating tape. A white crystalline sublimate, (0.13 g.) m.p. 96°C. collected in tube (b), and was transferred under nitrogen to a two-necked flask.

Analysis as isopropylideneaminodimethylaluminium dimer, $(Me_2AlN{=}CMe_2)_2$.

(Found: Al, 24.0; Me, 26.8%; M, 229. $(C_5H_{12}AlN)_2$ requires Al, 23.9; Me, 26.5%; M, 226).

Fig. 1a



Hydrolysis of some of this dimer with dilute acid gave acetone which was identified by its 2.4.dinitrophenylhydrazine derivative. When the hydrolysis was carried out with water an alkaline gas was liberated which was identified by its infrared spectrum as ammonia.

$(Me_2AlN{=}CMe_2)_2 + 8H_2O = 4MeH + 2Al(OH)_3 + 2NH_3 + 2Me_2CO.$

The nuclear magnetic resonance spectrum of the compound dissolved in carbon tetrachloride was recorded and showed only two peaks.

Peak 1. -128 c/s (_cf_. to T.M.S.)

Peak 2. +56 c/s (" " ")

The infrared spectrum was recorded as a nujol mull and as a KBr disc. There were only a few bands which are listed below: 3330 vw, 2990 w, 2920 ms, 2880 w, 1715 (sh), 1656 s, 1433 m(br), 1366 ms, 1235 ms, 1181 ms, 1087 w, 1075 w, 1010 w, 833 m(br), 722 ms(br), 684 s(br), 553 w(br), 465 m(br) cm.$^{-1}$

The conditions of the thermal decompositions of the adduct were varied, and the yields of the rearranged compound were measured. The results are summarised in the following table.

Table 1a

Amount of adduct $MeCN,AlMe_3$	Solvent	Time for reaction (hours)	Temperature °C.	Amount of methane given off	Yield of $(Me_2AlN=CMe_2)_2$
10.9 g.	30 c.c. of methyl cyclohexane	3	100	300 c.c.	none
0.69 g.	None. Sealed tube	5	150	80 c.c.	0.13 g. 19%
1.07 g.	None. Sealed tube	5	120	91 c.c.	0.15 g. 15%

Residue

Analysis of the yellow-brown residue in the flask showed the methyl to aluminium ratio as ca. 1.6:1 (Al, 23.4; Me, 21%). Hydrolysis with 80% sulphuric acid gave some acetone and ammonia but no methyl cyanide or acetic acid was detected in the spectra of the gases produced. The spectrum of the residue itself showed broad bands at ca. 2220 and 1670 cm.$^{-1}$

Formation of the ethyl cyanide adduct, EtCN.AlMe$_3$

A weighed amount of trimethylaluminium (ca. 1.5 g.) was condensed into a small two-necked flask together with an excess of ethyl cyanide. After a few minutes to allow the mixture to reach room temperature the excess of ethyl cyanide was removed by pumping, leaving a colourless crystalline solid m.p. 30°C. which could be purified by sublimation/distillation under vacuum.

Found: Al, 20.9; Me, 35.5%; M. 136. $C_6H_{14}AlN$ requires Al, 21.3; Me, 35.5%; M. 127.

The infrared spectrum which was recorded of the solid between KBr discs showed bands in the ν(C≡N) region at 2325 vs and 2245 w cm.$^{-1}$ The compound was again extremely sensitive to air and moisture.

Thermal decomposition of the trimethylaluminium-ethyl cyanide adduct - formation of s-butylideneaminodimethylaluminium dimer, $(Me_2AlN{=}CMeEt)_2$

Trimethylaluminium (0.9607 g., 13.3 m.mole) and ethyl cyanide (0.734 g., 13.3 m.mole) were condensed into a tube fitted with a fragile-tipped side arm and sealed under vacuum. The tube was heated in an oven at ca. 170°C. for one hour when the contents turned a dark red-brown colour. It was allowed to cool and was then attached by the side arm to the vacuum system where methane (115 c.c., 5.13 m.mole) was collected. The tube was then filled with nitrogen and fitted up as shown in Fig. 1. At 60°C. and ca. 0.01 mm. pressure a white crystalline solid, m.p. 73°C. was sublimed out. (Yield: 0.44 g., 26%).

Found: Al, 21.4; Me, 23.4%; M, 261. $C_{12}H_{28}Al_2N_2$ (as s-butylideneaminodimethylaluminium dimer) requires Al, 21.3; Me, 23.6%; M, 254.

Hydrolysis of the compound with dilute acid gave ethylmethyl ketone which was identified by its 2.4.dinitrophenylhydrazine derivative.

$$(Me_2AlN{=}CMeEt)_2 + 8H_2O = 4MeH + 2Al(OH)_3 + 2NH_3 + 2MeEtCO.$$

The infrared spectrum, recorded using a KBr disc, is compared in Table 2a with that of isopropylideneaminodimethylaluminium.

The nuclear magnetic resonance spectrum was recorded in solution using benzene and carbon tetrachloride as solvents, and tetramethylsilane as internal reference.

Results in benzene solution (cf. to T.M.S.)

Peak 1 (quartet); $\delta_{CH_2-CH_3}$ -112.9 cycles seconds^{-1}; J 7.9 c/s
Peak 2 (triplet); $\delta_{CH_3-CH_2}$ -47.3 c/s; J 7.6 c/s
Peak 3 (singlet); δ_{CH_3-C} -103 c/s
Peak 4 (singlet); $\delta_{(CH_3)_2Al}$ + 26 c/s

Residue

The residue (0.0867 g.) was hydrolysed with 2N-sulphuric acid to give methane; 1.78 moles of methane per mole aluminium (Al, 20.7; Me, 20.1%). The infrared spectrum of the residue showed a broad band at ca. 2220 cm^{-1} indicating (C=N) but ethyl cyanide was not found in the hydrolysis products. Ethylmethyl ketone and ammonia were shown to be present by infrared spectra on the vapours produced in the hydrolysis. Another sample of residue (0.1 g.) was boiled for two hours with 40% caustic soda, acidified and extracted with ether. No propionic acid was found on evaporating the ether solution.

Formation of the phenyl cyanide adduct, $PhCN.AlMe_3$

To trimethylaluminium (0.5 g., 7 m.mole) condensed in a two-necked flask, an equivalent amount of phenyl cyanide was added after the flask had been filled with dry, oxygen-free nitrogen. Immediately a colourless crystalline adduct was formed m.p. 80°C. This was removed under nitrogen to a Schlenk tube where it was purified by vacuum sublimation, 80-90°C. at 0.01 mm. The sublimate was scraped out under a purging nitrogen flow into a small two-necked flask.

Found: Al, 15.4; Me, 25.8%; M, 169. $C_{10}H_{20}AlN$ requires Al, 15.4; Me, 25.7%, M, 175.

The compound reacts vigorously with air and moisture and the infrared spectrum, recorded as a nujol mull made up in the glove box, showed bands at 2275 s and 2239 m cm^{-1} in the region where $\nu(C{\equiv}N)$ occurs.

Thermal decomposition of the trimethylaluminium-phenyl cyanide adduct - formation of 1-methylbenzylideneaminodimethylaluminium, $(Me_2AlN{=}CMePh)_2$

The adduct was prepared as above using trimethylaluminium (1.575 g., 21.9 m.mole) and phenyl cyanide (2.25 g., 21.8 m.mole). This was heated for four hours on an oil bath at 160-170°C. in the flask in which it had been prepared. An air condenser was fitted to the flask, (in case dissociation into the condensible Me_3Al and

PhCN occurred), but this did not seem necessary. The crude yellow glue which was left solidified on standing and its infrared spectrum was recorded as a KBr disc. This showed that reaction had taken place because no band was present around 2220 cm^{-1} but a new band appeared at ca. 1670 $cm.^{-1}$ The crude material was transferred to a double Schlenk tube where it was purified by sublimation under vacuum at 120°C. Apart from a few small drops of a liquid which appeared at the top of the tube the product was a pale yellow solid, m.p. 100°C. Not all of the material was allowed to sublime but the yield was over 50%.

Found: Al, 15.2; Me, 16.9%; M, 366. $C_{10}H_{20}AlN$ (as 1 methylbenzylideneaminodimethylaluminium dimer) requires Al, 15.4; Me, 17.1%; M, 350.

The product, as with the previous preparations, was much less air sensitive than the adduct; it is hydrolysed slowly in air and in water, but rapidly in dilute acid. From such a hydrolysis acetophenone was identified by its 2.4 dinitrophenylhydrazine derivative.

$$(Me_2AlN{=}CPhMe)_2 + 8H_2O = 4MeH + 2Al(OH)_3 + 2NH_3 + 2MePhCO$$

The infrared spectrum was recorded as a KBr disc and is compared in Table 2a to the other compounds.

Table 2a

$(Et_2AlNCMeEt)_2$ Liq. film cm.$^{-1}$	$(Me_2AlNCMe_2)_2$ Disc (KBr) cm.$^{-1}$	$(Me_2AlNCMePh)_2$ Disc (KBr) cm.$^{-1}$	$(Me_2AlNCMeEt)_2$ Disc (KBr) cm.$^{-1}$
3310 w	3330 vw	3280 vw	3320 vw
		3090 w	
		3060 w	
2960 s	2990 w	3330 w	2980 m
2920 s	2920 ms	2920 ms	2920 s
2880 s	2880 w	2880 m	2880 m
2850 s		2820 w	
2780 m			
2710 w			
	1715 (sh)		
1650 vs	1656 s	1634 vs	1659 vs
		1572 m	
		1493 m	
1456 s		1443 m	1460 m
1433 (sh)	1433 w(br)	1435 (sh)	1428 mw
1403 s			1420 (sh)
		1383 w	
1361 s	1366 ms	1361 m	1367 m
1305 wm		1307 vw	1328 mw

Table 2a(cont'd)

$(Et_2AlNCMeEt)_2$ Liq. film $cm.^{-1}$	$(Me_2AlNCMe_2)_2$ Disc (KBr) $cm.^{-1}$	$(Me_2AlNCMePh)_2$ Disc (KBr) $cm.^{-1}$	$(Me_2AlNCMeEt)_2$ Disc (KBr) $cm.^{-1}$
1261 m		1289 m	1269 m
1221 (sh)	1235 ms	1266 s	1214 s
1208 s			
1186 m	1181 ms	1179 s	1180 vs
1100 m	1087 w		1102 mw
1068 m	1075 w	1085 w	1177 mw
985 s	1010 vw	990 mw	969 w
948 s			950 m
917 m			
862 w			
837 w	833 m (br)		
826 w			800 (sh)
787 m		760 s	788 s
699 s	722 m(br)	718 s	715 s(br)
637 s(br)	684 s(br)	675 s	683 s(br)
		588 w	
		565 w	
529 m(br)	553 w(br)		553 m(br)
472 m(br)	465 m(br)		473 m(br)

Reactions of triphenylaluminium

Formation of the methyl cyanide adduct, $MeCN.AlPh_3$

Triphenylaluminium etherate (10.2 g., 30.5 m.mole) was dissolved in 25 c.c. of dry benzene contained in a flask filled with dry nitrogen and fitted with a distillation head. To this solution methyl cyanide (1.5 g., 35.6 m.mole), an excess over the equimolar quantity, was added. The mixture was then heated to 70-80°C. when the ether distilled off (2.25 g.) with a little of the benzene. The benzene solution was transferred to a Schlenk tube and pumped until all the benzene was removed. This left a white solid, m.p. 138°C., which was recrystallised from methylcyclohexane and again pumped dry.

Found: Al, 9.0; N, 4.8; C, 77.1; H, 6.3%; M, 303, 316.
$C_{20}H_{18}AlN$ requires Al, 9.0; N, 4.7; C, 80; H, 6.0%; M, 299.

The infrared spectrum was recorded as a nujol mull and in the $\nu(C{\equiv}N)$ region, bands occurred at 2305 w and 2275 s cm.$^{-1}$

Thermal decomposition of the triphenylaluminium-methyl cyanide adduct - formation of 1-methylbenzylideneaminodiphenylaluminium, $(Ph_2AlN{=}CMePh)_n$

A sample of the adduct prepared as described above was placed in a tube and heated while being pumped under a high vacuum. At ca. 200°C. a white crystalline solid sublimed to the cooler part of the tube and after about six hours the tube was cooled and filled with nitrogen. The solid at the top of the tube was transferred under an atmosphere of nitrogen to a two-necked flask; yields were in the range 10-15%.

For analysis the compound was allowed to react with dry hydrogen chloride and the benzene produced was weighed.

Found: Al, 9.2; N, 4.8; Ph, 51.2%. $C_{20}H_{18}AlN$ as 1-methylbenzylideneaminodiphenylaluminium requires Al, 9.0; N, 4.7; Ph, 51.5%.

The compound was too insoluble in benzene or nitrobenzene for either cryoscopic or ebullioscopic molecular weight measurements to be carried out.

On hydrolysis with dilute hydrochloric acid acetophenone was produced which was identified as its 2.4.dinitrophenylhydrazine derivative by melting point and infrared spectrum.

The infrared spectrum was recorded using a nujol mull; the bands are listed below:

1621 s, 1597 (sh), 1570 w, nujol band, 1414 m, nujol band, 1290 m, 1269 m, 1244 w, 1152 w, 1087 s, 1078 s, 1022 w, 987 w, 926 w, 844 w, 762 s, 724 s, 711 s, 699 s, 685 s, 673 s, 619 w, 599 m, 581 s, 503 w(br), 476 m(br), 461 s(br) cm.$^{-1}$

Formation of the phenyl cyanide adduct, $PhCN,AlPh_3$

Triphenylaluminium etherate (10 g., 30 m.mole) was dissolved in 25 c.c. of dry benzene. To this solution, which was again contained in a flask fitted with a distillation head and filled with an atmosphere of dry nitrogen, phenyl cyanide (4 g., 39 m.mole), a slight excess over the equimolar quantity, was added. The mixture was allowed to warm slowly to *ca.* 60°C. for a while before the ether from the etherate and a small amount of benzene was distilled off. The solution was transferred to a double Schlenk tube and the rest of the benzene was removed by a vacuum pump leaving a white crystalline solid. The solid was fairly soluble in hot methylcyclohexane and was recrystallised from this solvent.

Found: Al, 7.5; Ph, 63.0%; M, 375. $C_{25}H_{20}AN$ requires Al, 7.5; Ph, 63.9%; M, 361.

The infrared spectrum of the material was recorded both as a KBr disc and in nujol; in the $\nu(C\equiv N)$ region a strong band occurred at 2266 $cm.^{-1}$

Thermal decomposition of the triphenylaluminium-phenyl cyanide adduct - formation of 1-phenylbenzylideneaminodiphenylaluminium, $(Ph_2AlN{=}CPh_2)_n$

The adduct, $PhCN,AlPh_3$ (ca. 3 g.) was placed in a tube attached to the vacuum system so that any condensible gas passed into a U-trap cooled in liquid air. On heating the solid to about 240-250°C. it sublimed slowly giving a white crystalline solid, m.p. 295°C., yield 15%, and a few drops of a liquid which condensed in the upper part of the tube. A small quantity of liquid (ca. 0.1 c.c.) also condensed in the liquid air trap. The solid was transferred in the glove box to a two-necked flask.

Found: Al, 7.6; Ph, 42.8%. $C_{25}H_{20}AlN$ as 1-phenylbenzylideneaminodiphenylaluminium requires Al, 7.5; Ph, 42.7%.

The compound was too insoluble in benzene and nitrobenzene for cryoscopic molecular weight measurements to be carried out.

Infrared spectra showed the small amount of liquid in the liquid air trap to be benzene and the material at the top of the sublimation tube to be benzophenone.

Hydrolysis of the compound with dilute acid gave benzophenone identified as its 2.4 dinitrophenylhydrazine derivative.

The infrared spectrum was recorded using a KBr disc and a nujol mull. Bands from KBr disc are:

3049 m, 2985 m, 1658 vw, 1613 (sh), 1595 s, 1567 s, 1488 m, 1479 m, 1445 s, 1416 s, 1361 s, 1316 m, 1289 m, 1266 s, 1247 m, 1190 m, 1155 m, 1089 s, 1080 s, 1024 m, 1000 m, 951 s, 919 m, 909 s, 889 m(br), 862 w, 840 w, 787 s, 762 m, 729 s, 700 vs(br), 680 s, 620 s, 561 s, 481 s(br), 456 w(br) cm, $^{-1}$

and from the nujol mull are:

1618 (sh), 1595 s, 1570 m, nujol band, 1416 m, nujol band, 1316 w, 1289 m, 1263 m, 1245 m, 1189 w, 1152 w, 1088 s, 1081 s, 1022 w, 1000 w, 952 m, 920 m, 909 m, 862 w, 840 w, 788 s, 729 s, 699 vs, 682 s(br), 676 s, 626 m, 578 m, 481 s(br) cm. $^{-1}$

Reactions of dimethylaluminium hydride

The reaction of dimethylaluminium hydride with methyl cyanide - formation of ethylideneaminodimethylaluminium, $(Me_2AlN{=}CHMe)_n$

A solution of dimethylaluminium hydride in methylcyclohexane (5 c.c. of solution containing ca. ·1 g. per c.c.) was placed in a small two-necked flask filled with nitrogen. This was frozen in liquid air and methyl cyanide (0.5 g.) was added. The mixture was then allowed to warm up and it became quite hot, ca. 50-60°C. The flask was then attached to the vacuum system and the methylcyclohexane and unchanged methyl cyanide were pumped out. This left a colourless liquid, of which the infrared spectrum showed strong bands at ca. 1670 $cm.^{-1}$ The liquid, after standing overnight, turned slightly yellow and was distilled under vacuum (70-80°C., 0.05 mm.) but the colourless distillate solidified as a pale yellow glass.

A second sample was prepared exactly as described and analysed without any purification.

Found: Al, 26.4; Me, 30%; M, 220, 245 (conc. solution), 290, 304 (dilute solution). $C_4H_{10}AlN$ as ethylideneaminodimethylaluminium requires Al, 27.2; Me, 30.3%, M, dimer 198, trimer 297.

The compound was hydrolysed very rapidly in moist air; when hydrolysed with dilute acids it gave acetaldehyde, characterised by its 2.4 dinitrophenylhydrazine and dimedone derivatives.

The infrared spectrum was recorded of a thin film between KBr discs. The following bands were found: 3520 vw, 3260 vw, 2977 (sh), 2925 s, 2880 s, 2825 w, 1690 vs, 1640 s, 1432 m, 1397 w, 1361 m, 1259 w, 1190 s, 1123 m, 1059 w, 1037 w, 1005 w, 817 (sh), 784 s(br), 690 s(br), 560 w(br), 457 w(br) $cm.^{-1}$

The reaction of dimethylaluminium hydride with phenyl cyanide - formation of benzylideneaminodimethylaluminium dimer, $(Me_2AlN{=}CHPh)_2$

A solution of dimethylaluminium hydride in methylcyclohexane (5 c.c. of solution containing ca. 0.1 g. per c.c.) was added to phenyl cyanide (1 g., 10 m.mole) cooled by liquid air and contained in a nitrogen filled two-necked flask. The solution was allowed to warm up and became quite hot (50°C.); on cooling white crystals, m.p. 143°C., appeared. The solvent was then pumped off and the crystals were transferred to a sublimation tube where they sublimed at ca. 140°C. and 0.01 mm. pressure, (yield > 90%).

Found: Al, 16.4; Me, 18.6%; M, 329. $(C_9H_{12}AlN)_2$ as benzylideneaminodimethylaluminium dimer requires Al, 16.8; Me, 18.6%; M, 322.

The compound was hydrolysed easily by water and dilute acid.

Benzaldehyde was identified among the hydrolysis products as its phenylhydrazine derivative.

$$(Me_2AlN{=}CHPh)_2 + 8H_2O = 4MeH + 2Al(OH)_3 + 2NH_3 + 2PhHCO$$

The infrared spectrum was recorded in nujol and the bands are listed below:

1683 w, 1630 vs, 1595 s, 1580 s, 1496 w, 1452 s, 1411 m, 1380 w, 1333 vw, 1313 m, 1290 m, 1203 s, 1183 vs, 1101 vw, 1077 m, 1023 m, 1001 w, 967 m, 913 w, 840 vs, 745 vs, 685 vs(br), 615 w, 575 m(br), 470 w(br) $cm.^{-1}$

Reactions of triethylaluminium

Formation of the methyl cyanide adduct, $MeCN,AlEt_3$

Methyl cyanide (0.30 g., 7.3 m. mole) was placed by syringe in a nitrogen filled flask and then cooled to its freezing point by liquid air. To this triethylaluminium (0.82 g., 7.2 m. mole) was slowly added also by syringe. The contents of the flask were allowed to warm up to room temperature and pumped to remove any unused methyl cyanide; the product was a colourless liquid, f.p. -6°C.

Found: Al, 16.9; Et, 54.7%; M, 149. $C_8H_{18}AlN$ requires Al, 17.4; Et, 56.1%; M, 155.

Vapour pressure measurements in the range 22-68°C. are given by the equation $\log_{10}P_{mm.} = -2020/T + 7.38$, to within ± 1 mm. which corresponds to a value of 3.9 mm. at 25°C.

The compound was extremely sensitive to air and moisture so that the sample for the infrared spectrum was made up in the glove box. In the region of the C≡N stretching frequency there were bands at 2317 w, 2290 m, and 2253 w cm^{-1}.

Thermal decomposition of the triethylaluminium-methyl cyanide adduct - formation of s-butylideneaminodiethylaluminium dimer, $(Et_2AlN{=}CMeEt)_2$.

A sample of the adduct, $MeCN,AlEt_3$ (0.6582 g., 4.24 m. mole) was heated under vacuum at 110°C. at which temperature ethane (48.5 c.c., 2.16 m. mole) was evolved. The temperature was increased to 200°C. but very little more ethane was evolved. At about 210°C. under 0.01 mm. pressure a colourless liquid refluxed in the vessel. The vessel was cooled and filled with nitrogen and then attached to a receiver. After the apparatus had been pumped out again the liquid was distilled into the receiver at a bath temperature of 220°C. The product was a pale yellow liquid, 0.12 g., ca. 18% yield.

Found: Al, 17.6; Et, 38.6%; M, 328, 334. $(C_8H_{18}AlN)_2$ as s-butylideneaminodiethylaluminium dimer requires Al, 17.4; Et, 37.4%; M, 310.

Hydrolysis with dilute acid gave ethylmethyl ketone identified as its 2.4 dinitrophenylhydrazone whereas hydrolysis with water gave ammonia.

$$(Et_2AlN{=}CMeEt)_2 + 8H_2O = 4EtH + 2Al(OH)_3 + 2NH_3 + 2EtMeCO$$

The compound was very sensitive to air and moisture and becomes viscous and discoloured on standing. A sample was taken in the glove box for an infrared spectrum to be recorded as a thin film between KBr discs. The bands are listed in Table 2a.

The residue left in the flask after the product was distilled out was a red-black crisp solid insoluble in benzene, actone, methyl cyanide, pyridine and ether but slightly soluble in hot tetrahydrofuran.

It evolved ethane on hydrolysis with water and dilute acid. The infrared spectrum was not obtainable because of the opacity of the disc along the whole region from 4000 to 400 cm.$^{-1}$

Formation of the adduct of phenyl cyanide, $PhCN.AlEt_3$

Phenyl cyanide (1.59 g., 15.5 m.mole) was added to triethylaluminium (1.8 g., 15.5 m.mole) cooled in a nitrogen filled flask. There was a considerable heat of mixing which warmed the mixture to 50-60°C. The flask was allowed to cool to room temperature and then pumped for a few minutes at 0.01 mm; this left a very pale yellow liquid.

Found: Al, 12.0; Et, 38.6%; M, 210. $C_{13}H_{20}AlN$ requires Al, 12.4; Et, 40.1%; M, 217.

The infrared spectrum, recorded as a thin film between KBr discs, showed bands in the $\nu(C\equiv N)$ region at 2270 s and 2235 w cm.$^{-1}$

Thermal decomposition of the triethylaluminium-phenyl cyanide adduct - formation of benzylideneaminodiethylaluminium dimer, $(Et_2AlN=CHPh)_2$

Several reactions were carried out. In a typical example triethylaluminium (2.5 g., 22 m.mole) and phenyl cyanide (2.3 g., 23 m.mole) were transferred by syringe to a two-necked nitrogen filled flask fitted with an air-cooled condenser. The flask was then heated on an oil bath and the pale yellow adduct gradually turned darker. At about 190°C. there was a sudden rush of gas, (300 c.c. of ethylene identified by its infrared spectrum), from the flask and some of the mixture began to reflux. On heating for another hour more ethylene (ca. 150 c.c.) was eliminated, which corresponded to approximately one mole of ethylene per mole of adduct.

$$n\ Et_3AlNCPh = (Et_2AlN{=}CHPh)_n + nC_2H_4$$

The flask was cooled leaving a dark red glue. The air condenser was removed from the flask and a distillation head, thermometer and receiver were fitted. The apparatus was connected to the vacuum system and pumped out. The flask was heated in a silicone oil bath and at 160°C. and 0.05 mm. pressure, (oil bath, 200-210°C.), a pale yellow viscous liquid distilled off.

Found: Al, 13.8; Et, 30.4%; M, 420. $(C_{11}H_{16}AlN)_2$ as benzylideneaminodiethylaluminium dimer requires Al, 14.3; Et, 30.7%; M, 378.

The compound was hydrolysed with dilute acid and from the product the 2.4 dinitrophenylhydrazone and the phenylhydrazone of benzaldehyde were obtained.

$$(Et_2AlN{=}CHPh)_2 + 8H_2O = 4EtH + 2Al(OH)_3 + 2NH_3 + 2PhCHO$$

The infrared spectrum was recorded using a thin film of the liquid between KBr discs. The following bands were found: 3268 w, 3050 m, 3020 m, 2925 s, 2779 m, 1690 m, 1633 vs, 1600 s, 1582 s, 1494 m, 1456 s, 1408 s, 1373 m, 1311 s, 1282 s, 1228 s, 1203 s, 1192 m, 1177 m, 1160 w, 1102 w, 1076 m, 1053 w, 1020 w, 984 s, 945 s, 914 s, 840 s, 811 w, 778 s, 748 s, 702 vs, 676 vs(br), 625 vs(br), 540 s(br), 468 m(br) $cm.^{-1}$

Reactions of dimethylaluminium chloride

Formation of the methyl cyanide adduct, MeCN,$AlMe_2Cl$

Dimethylaluminium chloride (2 g., 15 m.mole) was transferred by syringe into a two-necked flask filled with nitrogen, (a drop of the liquid on the end of the syringe needle burned vigorously as the syringe was moved from the storage vessel to the flask). To this methyl cyanide (0.65 g., 15.9 m.mole) was added. There was an immediate reaction; the contents of the flask warmed and a white solid appeared. The flask was connected to the vacuum system and unchanged methyl cyanide pumped off. The solid was transferred from the flask under nitrogen to a sublimation tube where the compound sublimed at 70°C and 0.05 mm. pressure, m.p. 73°C.

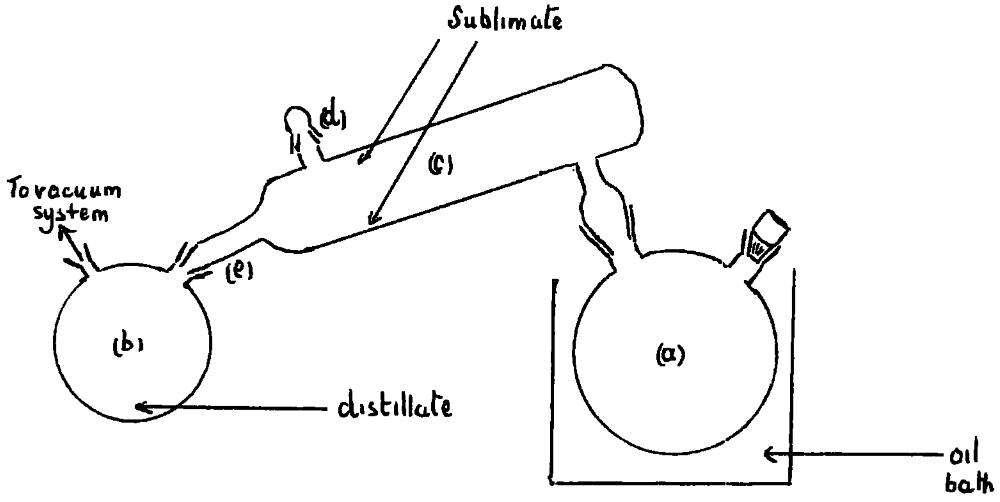
Found: Al, 20.0; Me, 22.3; Cl, 27.0%: M, 139. C_4H_9AlClN requires Al, 20.2; Me, 22.4; Cl, 26.6%; M, 133.5.

The spectrum was recorded as a nujol mull and bands in the region of the C≡N stretching frequency occurred at 2217 (sh), 2299 s, and 2259 w $cm.^{-1}$

Thermal decomposition of dimethylaluminium chloride-methyl cyanide adduct - formation of isopropylideneaminomethylaluminium chloride, $(Me_2C{=}NAlMeCl)_n$

Several reactions were carried out under various conditions and are summarised in Table 3a. In a typical case dimethylaluminium chloride (10 g., 108 m.mole) was placed in a two-necked nitrogen-filled flask, together with methyl cyanide (4.4 g., 106 m.mole). The flask was heated slowly on an oil bath to 150°C. taking ten minutes and then the temperature was raised very slowly to 160-165°C. At this point the contents, which had then liquified, started evolving a gas and the bunsen burner was removed from under the oil bath. The gas evolution became more vigorous, the material frothed up in the flask and about 2.5 litres of methane were collected during about a minute. The flask was then connected to an air condenser and receiver as shown in Figure 2a. At about 80-100°C. a colourless liquid distilled off and was collected in flask (b), and at 150°C. a white crystalline solid slowly sublimed out and collected in the air condenser (c).

Figure 2a



The apparatus was cooled and filled with nitrogen. Flask (b) was disconnected and stoppered. The condenser (c) was then disconnected from flask (a). Joint (d) was fitted into a small two-necked flask and the condenser (c) was purged with nitrogen while a spatula was pushed through neck (e) and used to scrape the solid through (d) into the flask. The yield of solid was about 0.25 g. (ca. 2%) m.p. 97°C.

Characterisation of the solid

Found: Al, 19.8; Me, 11.4%. C_4H_9AlClN as isopropylideneaminomethylaluminium chloride requires Al, 20.2; Me, 11.3%.

The solid was too insoluble in benzene for molecular weight measurements to be carried out. The infrared spectrum using both a nujol mull and a KBr disc was poor because the waxy nature of the solid made it very difficult to grind it sufficiently; in the ν (C=N) region bands occur at 1695 s and 1640 m $cm.^{-1}$

Hydrolysis with dilute nitric acid gave a solution which was shown to have chloride ion present with silver nitrate, and acetone which was identified as its 2.4 dinitrophenylhydrazine derivative.

$$(Me_2C{=}NAlMeCl)_n + 4nH_2O = nMeH + nAl(OH)_3 + nNH_4Cl + nMe_2CO$$

Characterisation of the liquid

The material was distilled at 80°C under vacuum before the analysis was carried out (yield ca. 1 g., 7%).

Found: Al, 20.9; Me, 11.6%; M, 299. C_4H_9AlClN as $(Me_2C{=}NAlMeCl)_n$ requires Al, 20.2; Me, 11.3%; M (for dimer) 267.

Hydrolysis of the compound gave ammonia and acetone. When hydrolysed with nitric acid, chloride ion was shown to be present with silver nitrate. The infrared spectrum was recorded as a thin film between KBr discs. The following bands were found: 3300 w, 2925 s, 2882 m, 2850 w, 2825 w, 1673 (sh), 1651 vs, 1590 w, 1433 m, 1369 s, 1259 m, 1239 s, 1191 s, 1076 m, 1059 m, 973 w, 875 m, 844 s, 813 (sh), 735 s(br), 697 s(br), 565 m(br) $cm.^{-1}$

Table 3a

Amount of Adduct	Vessel	Temp. °C.	Time hrs.	Methane off in c.c.	Adduct recovered	Products
2.2 g.	Sealed tube	110	28	97	1.06 g.	Brown polymer
0.8 g.	"	140	18	100	none	" "
6 g.	"	210	6	Large amount	"	Black solid
6 g.	Flask	170	1	980	"	Brown polymer Colourless liq. White solid
14.4 g.	"	165	0.5	2,500	"	"

Residue

The residue was similar to that from the reactions using trimethylaluminium. It was insoluble in benzene and ether but liberated methane on hydrolysis. The infrared spectrum showed some bands in the ν(C≡N) and in the ν(C=N) regions. Chloride was shown to be present in a solution in dilute nitric acid and a little acetone was found on hydrolysis.

Formation of the phenyl cyanide adduct, PhCN.AlMe$_2$Cl

Dimethylaluminium chloride (1.5 g., 16.2 m.mole) was transferred by syringe into a two-necked flask filled with nitrogen. To this phenyl cyanide (1.7 g., 16.5 m.mole) was added and the mixture warmed spontaneously leaving a moist white crystalline solid. The flask was attached to the vacuum line and pumped until the solid was dry. The solid was then removed and sublimed at 120°C. (0.01 mm.); the upper part of the sublimation tube was cooled with pieces of CO$_2$ because the compound supercooled and ran back down the tube. The pure compound had m.p. 83°C.

Found: Al, 13.7; Me, 15.6; Cl, 17.9%; M, 196. $C_9H_{11}AlClN$ requires Al, 13.8; Me, 15.4; Cl, 18.2%; M, 195.5.

The infrared spectrum was recorded as a nujol mull; in the ν(C≡N) region bands occurred at 2284 s and 2235 m cm.$^{-1}$

Thermal decomposition of dimethylaluminium chloride-phenyl cyanide adduct - formation of 1-methylbenzylideneaminomethylaluminium chloride, $(MeClAlN{=}CMePh)_2$

The adduct (6.2 g.) was heated in a flask on an oil bath for 20 hours at 170-180°C. After this time a brown-yellow viscous material was left which on standing set to a hard yellow solid. An infrared spectrum on this crude material showed a band at ca. 1670 $cm.^{-1}$ not present in the original adduct. The solid was then broken into lumps and transferred to a sublimation tube. It sublimed at 140°C. and 0.01 mm. to give a white solid, m.p. 135°C. The material underwent some decomposition and turned yellow after a few days so that it was not possible to resublime it, unlike most of the other compounds which were prepared.

Found: Al, 13.8 g.; Cl, 18.0; Me, 6.4; N, 7.0%; M, 397. $(C_9H_{11}AlClN)_2$ as 1-methylbenzylideneaminomethylaluminium chloride requires Al, 13.8; Cl, 18.1; Me, 7.7; N, 7.2%; M, 391.

The compound was hydrolysed with dilute acid which gave acetophenone identified as its 2.4 dinitrophenylhydrazone.

The infrared spectrum was recorded using a nūjol mull; the bands were as follows:

1619 s, 1603 (sh), 1572 m, 1453 m, 1296 w, 1271 m, 1188 m, 1088 w, 1025 w, 995 w, 922 w, 764 s, 722 s, 669 s(br), 635 w, 529 m(br), 443 m(br) $cm.^{-1}$

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