935. *Reactions of Organoaluminium Compounds with Cyanides. Part II.*[1] *Alkyl Cyanides*

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Adducts $\mathrm{RCN,AlR'_3}$ ($\mathrm{R} = \mathrm{Me}$ or $\mathrm{Bu^t}$, $\mathrm{R'} = \mathrm{Me, Et}$, or Ph), $\mathrm{RCN,AlMe_2Cl}$, and $\mathrm{EtCN,AlMe_3}$ have been prepared, and their rearrangement at 110—240° to the dimeric alkylideneamino-derivatives $\mathrm{(RR'C{:}N{\cdot}AlR'_2)_2}$ studied. The main decomposition reaction of the methyl and ethyl cyanide adducts involves cleavage of groups R′ from aluminium to give polymers such as $\mathrm{(R'_2AlCH_2CN)_n}$. Dimethylaluminium hydride with RCN gives $\mathrm{(RCH{:}N{\cdot}AlMe_2)_2}$ directly. The electronic and steric factors that appear to influence these rearrangements and the reactivity of the products are noted, and interpreted in terms of possible mechanisms. Features of the infrared spectra of these compounds are discussed, and the proton nuclear magnetic resonance (n.m.r.) spectra of several of the alkylideneamino-compounds are interpreted as evidence for *trans*-structures; a mixture of *cis*- and *trans*-isomers was obtained with $\mathrm{(MeCH{:}N{\cdot}AlMe_2)_2}$.

IN Part I,[1] some phenyl cyanide adducts $\mathrm{PhCN,AlR_3}$ were described and their rearrangement to benzylideneamino-derivatives $\mathrm{(PhCR{:}N{\cdot}AlR_2)_n}$ was discussed. The present Paper describes related adducts of methyl, ethyl, and t-butyl cyanides and their rearrangement to alkylideneamino-compounds $\mathrm{(R'CR{:}N{\cdot}AlR_2)_n}$, the only previously known example of which was n-butylideneaminodi-isobutylaluminium, $\mathrm{(PrCH{:}N{\cdot}AlBu^i_2)_n}$, v.p. 1 mm./161°, a reactive liquid of unknown molecular weight obtained by direct distillation of a 1 : 1 mixture of propyl cyanide and di-isobutylaluminium hydride.[2]

Alkyl Cyanide Adducts.—The adducts and their rearrangement reactions are listed in Table 1. The compounds $\mathrm{RCN,AlMe_3}$ ($\mathrm{R} = \mathrm{Me, Et}$, or $\mathrm{Bu^t}$), $\mathrm{R'CN,AlEt_3}$, and $\mathrm{R'CN,AlMe_2Cl}$ ($\mathrm{R'} = \mathrm{Me}$ or $\mathrm{Bu^t}$) were readily prepared by the exothermic reaction between equimolar quantities of nitrile and organoaluminium. The triphenylaluminium complexes $\mathrm{R'CN,AlPh_3}$ were prepared from the ether complex $\mathrm{Et_2O,AlPh_3}$ and only a slight excess of nitrile, a reaction that may reflect the relative volatilities of the two competing

TABLE 1

Thermal rearrangement of adducts $\mathrm{RCN,AlR'_3}$

		Decomposition				
Adduct	M. p.	Temp.	Reaction †	Non-polymeric product	M. p.	Yield (%)
$\mathrm{Bu^tCN,AlMe_3}$	61°	150°	Me$\rightarrow$	$\mathrm{(Bu^tCMe{:}N{\cdot}AlMe_2)_2}$	113°	95
$\mathrm{Bu^tCN,AlEt_3}$	<20	155—160	$\mathrm{C_2H_4}$, $\uparrow$H$\rightarrow$	$\mathrm{(Bu^tCH{:}N{\cdot}AlEt_2)_2}$	<20	80
$\mathrm{Bu^tCN,AlPh_3}$	114	170	Ph$\rightarrow$	$\mathrm{(Bu^tCPh{:}N{\cdot}AlPh_2)_2}$	dec. >220	85
$\mathrm{Bu^tCN,AlMe_2Cl}$ ...	84	240	Me$\rightarrow$	$\mathrm{(Bu^tCMe{:}N{\cdot}AlMeCl)_2}$	130	60
$\mathrm{Bu^tCN,AlMe_2H}$ *	—	<20	H$\rightarrow$	$\mathrm{(Bu^tCH{:}N{\cdot}AlMe_2)_2}$	89	90
$\mathrm{MeCN,AlMe_3}$	73	120—150	MeH, $\uparrow$Me$\rightarrow$	$\mathrm{(Me_2C{:}N{\cdot}AlMe_2)_2}$	96	15—20
$\mathrm{MeCN,AlEt_3}$	−6	110—130	EtH, $\uparrow$Et$\rightarrow$	$\mathrm{(MeCEt{:}N{\cdot}AlEt_2)_2}$	<20	18
$\mathrm{MeCN,AlPh_3}$	138	190—200	PhH, $\uparrow$Ph$\rightarrow$	$\mathrm{(MeCPh{:}N{\cdot}AlPh_2)_n}$	dec. >210	15
$\mathrm{MeCN,AlMe_2Cl}$ ...	73	160—165	MeH, $\uparrow$Me$\rightarrow$	$\mathrm{(Me_2C{:}N{\cdot}AlMeCl)_2}$ + $\mathrm{(Me_2C{:}N{\cdot}AlMeCl)_n}$	<20 97	7 4
$\mathrm{MeCN,AlMe_2H}$ *...	—	<20	H$\rightarrow$	$\mathrm{(MeCH{:}N{\cdot}AlMe_2)_2}$	<20	90
$\mathrm{EtCN,AlMe_3}$	30	160—170	MeH, $\uparrow$Me$\rightarrow$	$\mathrm{(EtCMe{:}N{\cdot}AlMe_2)_2}$	73	26

* Adduct itself not isolated, rearranging below room temperature. † In this column, $\uparrow$ indicates gas evolved, $\rightarrow$ indicates group or atom migrating.

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[1] Part I. J. E. Lloyd and K. Wade, *J.*, 1965, 2662.

[2] L. I. Zakharkin and I. M. Khorlina, *Doklady Akad. Nauk S.S.S.R.*, 1957, **116**, 422.

donor molecules rather than their relative donor strengths, as Mole has shown that in deuterochloroform solution phenyl cyanide only partly displaces co-ordinated ether from triphenylaluminium.[3] Alkyl cyanide adducts of dimethylaluminium hydride $RCN,AlMe_2H$ were not isolated; like the phenyl cyanide compound these rearranged rapidly at room temperature to give the products described below.

The alkyl cyanide adducts isolated decomposed rapidly in the presence of air or moisture, but were readily characterised by methods similar to those used for phenyl cyanide adducts. They were monomeric in benzene, and their infrared spectra contained bands characteristic of co-ordinated nitrile groups at frequencies some 30—60 cm.$^{-1}$ higher than the frequency of the free nitrile, as shown in Table 2. The increase, $\Delta\nu$, in the nitrile stretching frequency on co-ordination varies with the acceptor molecule, and follows a similar trend to that observed for related phenyl cyanide adducts. Values of $\Delta\nu$ for methyl cyanide complexes do not, in fact, differ significantly from the values for corresponding phenyl cyanide compounds, and can be interpreted in terms of increasing acceptor power $AlPh_3 < AlEt_3 < AlMe_3 = AlMe_2Cl$. In studies of nitrile complexes of inorganic halides, other workers have found that values of $\Delta\nu$ for complexes of phenyl cyanide were significantly lower than values for complexes of methyl cyanide.[4] This result was explained in terms of interaction between ring and nitrile orbitals in the phenyl cyanide adducts, allowing contribution from such canonical forms as $^{+}C_6H_5{=}C{=}N^{-}$. Our values of $\Delta\nu$ for the complexes of t-butyl cyanide are still higher than the values for the complexes of the other nitriles, and correspond to the series of increasing acceptor power $AlEt_3 = AlMe_3 < AlPh_3 < AlMe_2Cl$. As the frequency differences involved are small, too much significance should not be attached to their values, although the results are in general agreement with the sequence that would be expected from a consideration of the relative electronegativities of the groups attached to aluminium.

Table 2

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

		Acceptor molecule				
	Nitrile	—	$AlPh_3$	$AlEt_3$	$AlMe_3$	$AlMe_2Cl$
ν_{CN}	PhCN	2230 *	2265 †	2270 *	2273 †	2273 ‡
	MeCN	2253 *	2287 †	2290 *	2296 †	2296 †
	Bu^{t}CN	2235 *	2285 †	2282 *	2282 †	2293 †
$\Delta\nu$	PhCN	—	35	40	43	43
	MeCN	—	34	37	43	43
	Bu^{t}CN	—	50	47	47	58
ν_{AlN}	PhCN	—	411 †	394 *	391 †	412 ‡
	MeCN	—	408 †	402 *	401 †	412 †
	Bu^{t}CN	—	424 ‡	412 *	412 ‡	407 ‡

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

* Liquid film. † Nujol mull. ‡ Benzene solution.

Also listed in Table 2 are the frequencies of bands that are considered to be associated with the Al–N stretching vibration. A sharp band in the region 390—425 cm.$^{-1}$ is common to the spectra of all the adducts, but is absent from the spectra of the component nitriles and organoaluminium acceptor compounds. A band associated with the Al–N stretching vibration might be expected in this region by analogy with related compounds such as amine-aluminium hydride adducts [5] and amino-aluminium alkyls,[6] in the spectra of which bands near 500 cm.$^{-1}$ have been assigned to Al–N vibrations. Also ,the spectrum of the gallium trichloride complex $MeCN,GaCl_3$ contains a band at 335 cm.$^{-1}$, which has been calculated

[3] T. Mole, *Austral. J. Chem.*, 1963, **16**, 801.

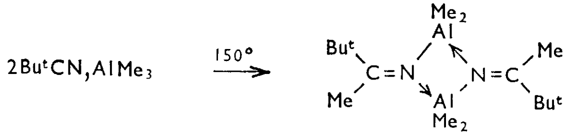
[4] H. J. Coerver and C. Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522; T. L. Brown and M. Kubota, *ibid.*, 1961, **83**, 4175.

[5] G. W. Fraser, N. N. Greenwood, and B. P. Straughan, *J.*, 1963, 3742.

[6] O. T. Beachley and G. E. Coates, *J.*, 1965, 3241; O. T. Beachley, G. E. Coates, and G. Kohnstam, *J.*, 1965, 3248.

to arise largely from a Ga–N stretching vibration.[7] The extent to which the band near 400 cm.$^{-1}$ in the spectra of our adducts may be regarded as due to an Al–N stretching vibration, however, is uncertain. Beattie and Gilson have recently shown that, in the spectrum of $(Me_3N)_2AlH_3$, a band near 200 cm.$^{-1}$ is more properly that designated ν_{Al-N}, the band at 460 cm.$^{-1}$ being mainly associated with deformation of the trimethylamine groups.[7] Thus, although an Al–N stretching vibration is considered to be involved in the vibration giving rise to the absorption near 400 cm.$^{-1}$ in the spectra of our nitrile complexes, it is not possible to draw any detailed conclusions from the precise value of the frequency of this band. Although the spectra of several of the nitrile complexes were recorded up to 200 cm.$^{-1}$, no other band attributable to ν_{Al-N} was found.

Rearrangement Reactions.—These are summarised in Table 1. The adducts of t-butyl cyanide rearranged in a similar manner to those of phenyl cyanide, forming dimeric alkylideneaminoalanes in good yield, *e.g.*,



The adduct of triethylaluminium lost ethylene at about 155—160°, and subsequent (or simultaneous) hydrogen transfer gave $(Bu^tCH{:}N{\cdot}AlEt_2)_2$ the neopentylideneamino-compound. Triethylaluminium itself loses ethylene[8] at about 160°, although by the reversible reaction $Et_3Al \rightleftharpoons Et_2AlH + C_2H_4$, so that the overall rate of decomposition appears slower than the irreversible decomposition of our nitrile adducts. When $Bu^tCN,AlEt_3$ was held at about 160°, some transfer of ethyl apparently occurred as well, the product having an extra band in the C:N region of the infrared spectrum at 1626 cm.$^{-1}$, the frequency at which such a band might be expected for the compound $(Bu^tCEt{:}N{\cdot}AlEt_2)_2$, but a pure sample of the latter was not isolated. It was found convenient to use a slightly higher temperature for the rearrangement of the triphenylaluminium adduct, although there seemed little difference between the migratory aptitudes of methyl and phenyl groups. However, the methyl groups of $Bu^tCN,AlMe_2Cl$ were markedly less mobile, a temperature of 240° being necessary for the rearrangement of this adduct. Other workers also have found the transfer of organic groups from alkylaluminium halides to occur less readily than the transfer of groups from the trialkyls.[9, 10] Hydrogen transfer occurred much more readily than alkyl or aryl transfer; dimethylaluminium hydride and t-butyl cyanide gave neopentylideneaminodimethylaluminium dimer when mixed at, or below, room temperature. Our results show that the readiness with which groups attached to aluminium migrate to the carbon of a cyanide group decrease in the sequence H (of $AlMe_2H$) $\gg$ Me (of $AlMe_3$) $\simeq$ Et (of $AlEt_3$) $>$ Ph (of $AlPh_3$) $>$ Me (of $AlMe_2Cl$), a sequence in which there appears to be decreasing negative charge on the migrating atom or group.

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

Methyl and ethyl cyanide differ from t-butyl and phenyl cyanides in having attached to the α-carbon atom hydrogen atoms that allow the possibility of acidic reaction. As a consequence, the thermal decomposition of their adducts with organoaluminium compounds

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[7] I. R. Beattie and T. Gilson, *J.*, 1964, 2292, 3528.

[8] A. W. Laubengayer and W. F. Gilliam, *J. Amer. Chem. Soc.*, 1941, **63**, 477; K. Ziegler, ch. 5, " Organometallic Compounds," ed. H. Zeiss, Reinhold, New York, 1960, p. 194.

[9] S. Pasynkiewicz, W. Dahlig, and B. Tomaszewski, *Roczniki Chem.*, 1962, **36**, 1383.

[10] H. Reinheckel and D. Jahnke, *Chem. Ber.*, 1964, **97**, 2661.

follows a different course, the main reaction involving cleavage of organic groups from aluminium, *e.g.*,

$$n\text{CH}_3\text{CN,AlR}_3 \longrightarrow (\text{R}_2\text{AlCH}_2\text{CN})n + n\text{RH}$$

Similar cleavage of organic groups from magnesium occurs in reactions between Grignard reagents and certain alkyl cyanides.[11] Thus, methane was evolved from methylaluminium adducts, ethane from the ethylaluminium compound and benzene from the phenyl compound when these were heated to the temperatures shown in Table 1. Once decomposition had started, very rapid evolution of gas occurred as the heat evolved raised the reaction temperature, so that generally the bulk of a sample of adduct was converted into a glue or glass within a minute; not all of a sample decomposed in this manner, however. The quantity of gas evolved was rarely more than 60% of that expected from the equation above, and small samples ($<20\%$) of alkylideneamino-compounds $(\text{MeCR:N}{\cdot}\text{AlR}_2)_n$ were recovered from the residue by vacuum sublimation, showing that a rearrangement reaction like that which occurs with phenyl or t-butyl cyanide adducts had also taken place, *e.g.*,

$$\text{MeCN,AlMe}_3 \longrightarrow 15\text{—}20\%\ (\text{Me}_2\text{C:N}{\cdot}\text{AlMe}_2)_2$$

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

The involatile glassy residues left after methyl cyanide adducts have decomposed, shown as $(\text{R}_2\text{AlCH}_2\text{CN})_n$ above, are apparently complex polymeric materials. They are insoluble in the common inert organic solvents, but are readily hydrolysed by dilute acids. Values of the R : Al ratio lie between 1 : 1 and 2 : 1, showing that some rearrangement as well as cleavage of groups R from aluminium has occurred, a conclusion supported by the presence of ketones in the hydrolysate and by bands characteristic of C=N groups as well as C≡N groups in the infrared spectra of the polymers.

Although adducts $\text{RCN,AlR}'_3$ do not rearrange appreciably at temperatures below 100°, Reinheckel and Jahnke [10] have shown that addition across the C⋮N link occurs at a lower temperature if the adduct is treated with an equimolar quantity of the organoaluminium compound:

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

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

When a 1 : 2 mixture of methyl cyanide and dimethylaluminium hydride was heated at 145° for 30 minutes, appreciable addition across the C:N *double* bond occurred.

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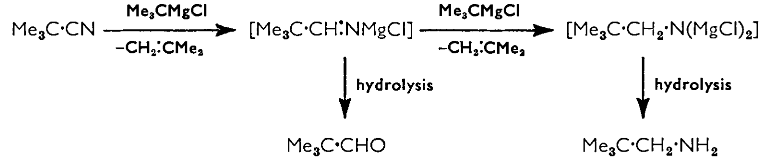
[11] M. S. Kharasch and O. Reinmuth, " Grignard Reactions of Nonmetallic Substances," Constable, 1954, p. 773.

Hydrolysis of the residual glue gave mainly methane and ethylamine and only small quantities of hydrogen and ammonia:

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

Partial reduction beyond the azomethine stage has already been observed in other reactions between a nitrile and an excess of an organometallic compound. For example, benzylamine is among the products when benzonitrile is treated with an excess of dibutylaluminium hydride[12] or tributylaluminium[13] (acting as a source of the hydride Bu_2AlH) and the reaction mixture is hydrolysed, while neopentylamine is formed in a similar reaction sequence involving t-butyl cyanide and the Grignard reagent[14] Bu^tMgCl at 150°;



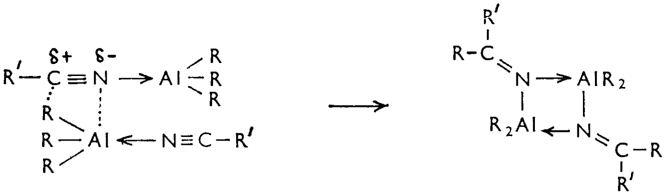
$$\begin{tikzcd} \mathrm{Me_3C{\cdot}CN} \arrow[r, "\mathrm{Me_3CMgCl}", "-\mathrm{CH_2{:}CMe_2}"'] & {[\mathrm{Me_3C{\cdot}CH{:}NMgCl}]} \arrow[r, "\mathrm{Me_3CMgCl}", "-\mathrm{CH_2{:}CMe_2}"'] \arrow[d, "\text{hydrolysis}"] & {[\mathrm{Me_3C{\cdot}CH_2{\cdot}N(MgCl)_2}]} \arrow[d, "\text{hydrolysis}"] \\ & \mathrm{Me_3C{\cdot}CHO} & \mathrm{Me_3C{\cdot}CH_2{\cdot}NH_2} \end{tikzcd}$$

It should be stressed that in such reactions an *excess* of the organometallic compound is needed, as only one of the groups originally attached to aluminium appears to be available for reaction. This may be contrasted with the behaviour of aluminium hydride itself, in which *two* hydrogen atoms per aluminium are available for transfer reactions, *e.g.*,[15]

$$\mathrm{MeCN + Et_3N,AlH_3} \longrightarrow [\mathrm{MeCH{:}N{\cdot}AlH_2}] \longrightarrow [\mathrm{MeCH_2NAlH}]$$

Two of the four hydrogen atoms of lithium aluminium hydride are similarly available for the reduction of nitriles to amines, although reaction can be stopped at the azomethine stage.[16, 17]

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



The observation already noted that the rearrangement occurs less readily if electronic charge is withdrawn from the migrating group is consistent with this. Further rearrangement of the alkylideneaminoalanes themselves could involve a similar mechanism, attack on the carbon of the azomethine group by the migrating group, and will therefore occur less readily, because of the increased steric hindrance about that carbon atom, because of the lower effective positive charge on it, and because of the greater withdrawal of electrons from the groups R′ attached to aluminium now that *two* nitrogen atoms are also attached to aluminium. The lack of further rearrangement of $(Bu^tCMe{:}N{\cdot}AlMe_2)_2$ at about 280°, or of attack by Me_3Al on this compound, contrasted with the reaction between $(MeCH{:}N{\cdot}AlMe_2)_2$ and $AlMe_2H$ at 145°, are all consistent with this interpretation of the factors influencing these reactions. The alkylideneamino-compounds, however, are also

[12] A. E. G. Miller, J. W. Biss, and L. H. Schwartzman, *J. Org. Chem.*, 1959, **24**, 627.
[13] K. Ziegler, K. Schneider, and J. Schneider, *Annalen*, 1959, **623**, 9.
[14] E. J. Blanz and H. S. Mosher, *J. Org. Chem.*, 1958, **23**, 492.
[15] R. Ehrlich, A. R. Young, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, 1964, **3**, 628.
[16] L. M. Soffer and M. Katz, *J. Amer. Chem. Soc.*, 1956, **78**, 1705.
[17] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1964, **86**, 1085.

susceptible to nucleophilic attack at the aluminium atoms, which can expand their co-ordination number above four. Those prepared in this work, although less sensitive to air and moisture than the adducts, still required manipulation in an atmosphere of nitrogen. The sensitivity was found to be least for those compounds that had most crowding of the groups about the aluminium atoms, the compound $(Bu^tCMe{:}N\cdot AlMe_2)_2$, for example, being hydrolysed too slowly by dilute acid to enable this method to be used for its analysis. All these aluminium compounds were much more readily hydrolysed than the related ethylideneaminoboranes, $(MeCH{:}N\cdot BR_2)_2$, in which the boron, already four-co-ordinate, cannot accommodate further donor molecules.[18]

The strong tendency of HAl groups to add across nitriles prompted the study of the reaction between dimethylaluminium hydride and hydrogen cyanide in hexane at —78° as a route to $(H_2C{:}N\cdot AlMe_2)_n$. Hydrogen was evolved, however, and tetrameric dimethylaluminium cyanide, $(Me_2AlCN)_4$, was produced. This compound has previously been prepared from trimethylaluminium and hydrogen cyanide.[19]

Features of the infrared spectra of the alkylideneamino- and benzylideneamino-aluminium derivatives are given in Table 3. All the spectra contain strong or very strong absorption bands in the region 1600—1675 cm.$^{-1}$ characteristic of the C:N stretching vibration, the frequency apparently being sensitive to the groups attached to the carbon, being highest for compounds with hydrogen or a small alkyl group attached to this carbon atom and lowest when t-butyl or phenyl groups are the substituents.

TABLE 3

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

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

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

* Liquid film. † Nujol mull. ‡ KBr disc. § CCl_4 solution. ¶ For a discussion of this assignment see ref. 1.

Another common feature of the infrared spectra is a band between 437 and 478 cm.$^{-1}$, which appears to be associated with a vibration of the $(AlN)_2$ ring. A band at 508 cm.$^{-1}$ has been shown[6] to be associated with a ring vibration in the spectrum of the aminoalane $(Me_2NAlMe_2)_2$, although the sensitivity of this band to deuteration of the dimethylamino group, when it moves to 482 cm.$^{-1}$, shows that movement of the rest of the molecule contributes to this absorption. Other bands between 450 and 500 cm.$^{-1}$ in some of the spectra, particularly those of phenyl or chloro-derivatives, make assignment uncertain in these instances, but the frequencies listed in Table 3 are those indicated by analogy with the less ambiguous methyl derivatives.

[18] J. E. Lloyd and K. Wade, *J.*, 1964, 1649.
[19] G. E. Coates and R. N. Mukherjee, *J.*, 1963, 229.

Seven of the compounds prepared contained $AlMe_2$ groups, and three others AlMeCl groups. Features of their spectra that are readily identified are also listed in Table 3. The dimethylalanes have a characteristic strong sharp band at 1181—1192 cm.$^{-1}$, due to the symmetrical deformation vibration of the methyl groups bound to aluminium, and a broad region of strong absorption around 700 cm.$^{-1}$, consisting of a strong or very strong band centred at 676—690 cm.$^{-1}$ with a shoulder or second band around 710—745 cm.$^{-1}$, which together can be attributed to Al–CH_3 asymmetrical stretching and rocking vibrations. A less intense peak at 550—582 cm.$^{-1}$ can be assigned to the Al–CH_3 symmetrical stretching vibration. These assignments are made on the basis of studies by Gray,[20] Hoffmann and Schomburg,[21] and Coates and his co-workers [6, 22] on various methylaluminium compounds.

The methylchloroaluminium compounds have a strong sharp band near 1190 cm.$^{-1}$ in their spectra [Al–CH_3 δ (sym)], and broad strong absorptions near 690 cm.$^{-1}$ and 570 cm.$^{-1}$ due to Al–CH_3 stretching and rocking vibrations. A band in the region 477—494 cm.$^{-1}$ can be assigned to the Al–Cl stretching vibration by analogy with Gray's assignments for methylaluminium chlorides.[20]

The proton magnetic resonance spectra (p.m.r.) of the alkylideneamino-derivatives were recorded, and τ values are listed in Table 4. Assignments were generally straightforward, and are indicated in the Table. It has previously been shown that p.m.r. spectra can be used to detect the presence of mixed isomers in such systems.[1,18] On the basis of the number of peaks corresponding to Al–Me or Al–Et groups, only one of the compounds described here appears to exist in the form of a mixture of *cis*- and *trans*-isomers, *viz.* $(MeCH{:}N{\cdot}AlMe_2)_2$, for which the peaks at τ 10·83 and 10·93 p.p.m. evidently arise from the *cis*-compound (I), the peak at τ 10·88 p.p.m. from the *trans*-compound (II). The boron analogues of these isomers are already known.[18]

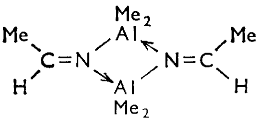
TABLE 4

Proton magnetic resonance spectroscopic results

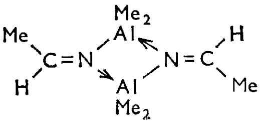
Compound	Solvent	τ values of peaks (p.p.m.; $\tau_{Me_4Si} = 10{\cdot}00$)			
		=C–H	=C–Me	=C–Et or =C–Bu^t	Al–Me or Al–Et
$(Me_2C{:}N{\cdot}AlMe_2)_2$	CCl_4	—	$7{\cdot}9_0$s(1)	—	$10{\cdot}9_3$s(1)
$(MeCH{:}N{\cdot}AlMe_2)_2$	CCl_4	$1{\cdot}6_0$q(1)	$7{\cdot}8_9$d(3)	—	$10{\cdot}8_3$s; $10{\cdot}8_8$s; $10{\cdot}9_3$s(6)
$(EtCMe{:}N{\cdot}AlMe_2)_2$	CCl_4	—	$7{\cdot}9_0$s(3)	$7{\cdot}6_7$q(2); $8{\cdot}8_0$t(3)	$10{\cdot}9_1$s(6)
$(EtCMe{:}N{\cdot}AlMe_2)_2$	C_6H_6	—	$8{\cdot}2_8$s(3)	$7{\cdot}9_9$q(2); $9{\cdot}2_1$t(3)	$10{\cdot}4_3$s(6)
$(Bu^tCMe{:}N{\cdot}AlMe_2)_2$	C_6H_6	—	$7{\cdot}8_4$s(1)	$8{\cdot}8_7$s(3)	$10{\cdot}3_4$s(2)
$(Bu^tCH{:}N{\cdot}AlMe_2)_2$	CCl_4	$5{\cdot}3_6$s(1)	—	$8{\cdot}8_8$s(9)	$10{\cdot}8_7$s(6)
$(Bu^tCH{:}N{\cdot}AlMe_2)_2$	C_6H_6	$4{\cdot}2_8$s(1)	—	$9{\cdot}1_4$s(9)	$10{\cdot}5_7$s(6)
$(Bu^tCH{:}N{\cdot}AlEt_2)_2$*	None	$1{\cdot}7_5$s(1)	—	$8{\cdot}9_1$s(9)	$8{\cdot}9_9$t(6); $10{\cdot}0_2$q(4)
$(Me_2C{:}N{\cdot}AlMeCl)_2$	CCl_4	—	$7{\cdot}7_3$c	—	10·6c
$(Me_2C{:}N{\cdot}AlMeCl)_2$	C_6H_6	—	$8{\cdot}6_3$c	—	$10{\cdot}3_7$c
$(Bu^tCMe{:}N{\cdot}AlMeCl)_2$	C_6H_6	—	$7{\cdot}8_5$d	$8{\cdot}9_7$s	$10{\cdot}1_6$s; $10{\cdot}2_4$s

* Internal standard, benzene ($\tau = 2{\cdot}73$); internal standard, tetramethylsilane in all other cases.

s = singlet, d = doublet, t = triplet, q = quartet; relative intensities in parentheses.



(I)



(II)

The isobutylideneamino-compound $(EtCMe{:}N{\cdot}AlMe_2)_2$, examined in both carbon tetrachloride and benzene solution, had only one peak attributable to $AlMe_2$, which would indicate that only the *trans*-isomer was present, unless the difference between the two types of $AlMe_2$ groups in the *cis*-form was insufficient to be detected. There is a noticeable solvent effect on the τ values for this compound.

[20] A. P. Gray, *Canad. J. Chem.*, 1963, **41**, 1511.

[21] E. G. Hoffmann and G. Schomburg, *Adv. Mol. Spectroscopy*, 1962, 804.

[22] G. E. Coates and R. N. Mukherjee, *J.*, 1964, 1295.

With the t-butyl compounds $(Bu^tCMe{:}N{\cdot}AlMe_2)_2$, $(Bu^tCH{:}N{\cdot}AlMe_2)_2$, and $(Bu^tCH{:}N{\cdot}AlEt_2)_2$, for which the p.m.r. spectra show the presence of only the *trans*-isomers, such a result is intelligible in that the bulk of the butyl groups might lead to bond-angle strain in a *cis*-isomer. The presence of only one isomer in the first two of these butyl compounds is also consistent with their crystalline form and the sharpness of their melting points.

The p.m.r. spectra of both the methylchloro-compounds $(Me_2C{:}N{\cdot}AlMeCl)_2$ and $(Bu^tCMe{:}N{\cdot}AlMeCl)_2$ were recorded, but were unexpectedly complex and could not be interpreted with certainty. Their p.m.r. spectra should not be sensitive to the relative orientation of the AlMeCl groups. However, the slow development of a yellow colour in the solutions of these compounds suggested that the complexity might be due to impurities resulting from decomposition of the samples or attack on the solvent or tetramethylsilane standard. The p.m.r. spectrum of the phenyl compound $(Bu^tCPh{:}N{\cdot}AlPh_2)_2$ in deuterotoluene was complex and could not be assigned with certainty; τ values of peaks were 3·07c, 3·52c, 4·27c, 9·93s p.p.m.

The apparent bond-angle strain in the $(AlN)_2$ ring of the dimeric alkylideneaminoalanes has already been remarked upon.[1] All the compounds obtained in the present work for which *M* has been determined by the cryoscopic method in benzene solution, however, have proved to be dimeric. (The waxy solid isomer of $(Me_2C{:}N{\cdot}AlMeCl)_n$, insoluble in the common solvents, may be polymeric.) In related amino-aluminium and -gallium compounds, considered to be dimeric in the crystal phase at room temperature, ring opening to polymeric structures occurs when they are heated, the resulting glasses softening to dimeric liquids over a short temperature interval as if melting.[6] No evidence of such a crystal $\longrightarrow$ glass $\longrightarrow$ liquid change was detected when certain of our compounds, for which p.m.r. spectroscopic evidence of the presence of only one isomer was available, were heated slowly to the melting point under a polarising microscope, even though the greater strain expected to be present in the alkylideneamino-compounds should make a transition to a polymeric glass more likely. One must conclude therefore, that bond-angle strain in our compounds is small.

EXPERIMENTAL

The organic cyanides were purified by distillation from phosphorus pentoxide, and the organoaluminium reagents were purified as described in Part I.[1] Most of the compounds described here were air- and moisture-sensitive. Details of the preparative, manipulative, and analytical procedures used for their study have already been given.[1]

Infrared spectra were recorded on Grubb–Parsons prism-grating spectrometers, the GS2A or Spectromaster in the range 2—25 μ, and the DB3/DM2 from 21 to 50 μ. Nuclear magnetic resonance spectra were recorded at 60 Mc. sec.$^{-1}$ on an A.E.I. R.S. 2 or a Perkin-Elmer spectrometer. Samples were in the form of approximately 20% solutions in carbon tetrachloride, benzene, or deuterotoluene with tetramethylsilane as internal standard. Molecular weights were determined cryoscopically in benzene solution.

Reactions of Methyl Cyanide.—(*a*) *Trimethylaluminium.* Methyl cyanide (3·52 g., 86 mmoles) and trimethylaluminium (6·40 g., 89 mmoles) mixed at −196° and allowed to warm, reacted exothermically to form a moist crystalline solid from which the colourless crystalline *adduct*, $MeCN,AlMe_3$, m. p. 73° was obtained by vacuum sublimation at about 70° (Found: Al, 23·7; hydrolysable methyl, 39·7%; *M*, 108. $C_5H_{12}AlN$ requires Al, 23·9; hydrolysable methyl, 39·8%; *M*, 113).

Thermal decomposition of $MeCN,AlMe_3$. A sample of adduct (0·68 g., 6·0 mmoles) was heated at 150° for 5 hr. in a sealed tube to form a gas, a colourless crystalline solid, which could be vacuum sublimed from the reaction tube at 90°, and an involatile yellow-brown glass. The gas was identified by its infrared spectrum as methane (3·6 mmoles). The crystalline solid was *isopropylideneaminodimethylaluminium dimer* $(Me_2C{:}N{\cdot}AlMe_2)_2$, m. p. 96° (0·13 g., 0·6 mmole) (Found: Al, 24·0; hydrolysable methyl, 26·8%; *M*, 229. $C_{10}H_{24}Al_2N_2$ requires Al, 23·9; hydrolysable methyl, 26·5%; *M*, 226); $\nu_{max.}$ (Nujol mull or KBr disc) 2985w, 2920s, 2882w, 1658s, 1430w, 1366ms, 1263vw, 1235ms, 1181ms, 1089w, 1075w, 1020vw, 836w, 800vw, 721s(sh), 682vs, 554w, and 465w-m cm.$^{-1}$. It reacted vigorously with water to form acetone, ammonia, and aluminium hydroxide. The involatile yellow-brown glass gave acetone, ammonia, aluminium hydroxide and methane on hydrolysis (Al, 23·4; hydrolysable methyl, 21·0%), but no methyl cyanide or acetic acid was detected. Its infrared spectrum contained broad bands at about 2300 and 1670 cm.$^{-1}$.

In other experiments on the decomposition of $\mathrm{MeCN,AlMe_3}$, the yield of rearranged material $(\mathrm{MeC{:}N{\cdot}AlMe_2})_2$ from the reaction at 120° was found to be slightly lower (15%). When the decomposition was carried out in boiling methylcyclohexane (100°), methane was evolved, but no isopropylideneamino-derivative was recovered.

When methyl cyanide (2·0 g.; 50 mmoles) and trimethylaluminium (7·5 g.; 102 mmoles) were heated in boiling benzene (80°) no methane was evolved. After 24 hr. the solvent was removed under vacuum, leaving a colourless viscous oil, which lost trimethylaluminium slowly on prolonged evacuation. The infrared spectrum of this oil, with a band at ~1660 cm.$^{-1}$ but not at 2300 cm.$^{-1}$, was very similar to that of $(\mathrm{Me_2C{:}N{\cdot}AlMe_2})_2$, but a pure sample of the latter was not isolated from this reaction.

(*b*) *Triethylaluminium.* Equimolar quantities of methyl cyanide and triethylaluminium react exothermically to give the liquid *adduct* $\mathrm{MeCN,AlEt_3}$, f.p. −6°, v.p. 3·9 mm./25° (Found: Al, 16·9; hydrolysable ethyl, 54·7%; *M*, 149. $\mathrm{C_8H_{18}AlN}$ requires Al, 17·4; hydrolysable ethyl, 56·1%; *M*, 155).

Thermal decomposition of $\mathrm{MeCN,AlEt_3}$. A sample of the adduct $\mathrm{MeCN,AlEt_3}$ (0·658 g., 4·24 mmoles) when heated to 110° evolved ethane (48·5 c.c., 2·16 mmoles). Further heating to 200° caused a little more ethane to be evolved, and enabled a colourless liquid (0·12 g.) to be vacuum-distilled from the reaction mixture. This liquid was identified as *diethyl-s-butylideneaminoaluminium dimer* $(\mathrm{EtCMe{:}N{\cdot}AlEt_2})_2$ (Found: Al, 17·6; hydrolysable ethyl, 38·6%; *M*, 331. $\mathrm{C_{16}H_{36}Al_2N_2}$ requires Al, 17·4; hydrolysable ethyl, 37·4%; *M*, 310); $\nu_{\text{max.}}$ (liquid film) 3310w, 2960s, 2920s, 2880s, 2850s, 2780m, 2710w, 1650vs, 1456s, 1433msh, 1403s, 1361s, 1305wm, 1261m, 1221sh, 1208s, 1186m, 1100m, 1068m, 985s, 948s, 917m, 862w, 837w, 826w, 787m, 702vs, 634vs(br), 529m, and 473m cm.$^{-1}$. It decomposed in air, was immediately hydrolysed by water, forming ammonia, ethane, ethyl methyl ketone, and aluminium hydroxide, and turned viscous and pale yellow in colour on prolonged standing under nitrogen. The involatile residue from the decomposition of $\mathrm{MeCN,AlEt_3}$, a red-black glass, evolved ethane when treated with water or dilute acid.

(*c*) *Triphenylaluminium-*(*diethyl ether*) *complex.* Methyl cyanide (1·5 g., 35·6 mmoles) and triphenylaluminium–ether complex (10·2 g., 30·5 mmole) were heated for 1 hr. under nitrogen in boiling benzene. Removal of the solvent left colourless crystals of the *adduct*, $\mathrm{MeCN,AlPh_3}$, m. p. 138° (from methylcyclohexane) (Found: C, 77·1; H, 6·3; Al, 9·0; N, 4·8%; *M*, 310. $\mathrm{C_{20}H_{18}AlN}$ requires C, 80·3; H, 6·0; Al, 9·0; N, 4·7%; *M*, 299).

Thermal decomposition of $\mathrm{MeCN,AlPh_3}$. Samples of the adduct when heated under vacuum to 200° lost benzene, and a colourless crystalline solid sublimed from the reaction mixture. This was identified as 1-*methylbenzylideneaminodiphenylaluminium*, $(\mathrm{PhCMe{:}N{\cdot}AlPh_2})_n$, decomposes >210° (Found: Al, 9·2; N, 4·8; Ph (by hydrogen chloride cleavage), 51·2%. $\mathrm{C_{20}H_{18}AlN}$ requires Al, 9·0; N, 4·7; Ph, 51·5) $\nu_{\text{max.}}$ (Nujol mull) 1621s, 1597s, 1290m, 1269m, 1244w, 1152w, 1087s, 1078s, 1022w, 987w, 926w, 844w, 762s, 724s, 711s, 699s, 685s, 673s, 619w, 599m, 581s, 503w(br), 476m(br), 461s(br) cm.$^{-1}$. This compound was too insoluble in benzene or nitrobenzene for cryoscopic or ebullioscopic determination of *M*. It was hydrolysed by dilute hydrochloric acid to acetophenone and benzene.

(*d*) *Dimethylaluminium chloride.* The *adduct* $\mathrm{MeCN,AlMe_2Cl}$, from equimolar quantities of the components, is a colourless crystalline solid, m. p. 73°, which can be purified by vacuum sublimation at 70° (Found: Al, 20·0; Cl, 27·0; hydrolysable methyl, 22·3; *M*, 139. $\mathrm{C_4H_9AlClN}$ requires Al, 20·2; Cl, 26·6; hydrolysable methyl, 22·4%; *M*, 133·5).

Thermal decomposition of $\mathrm{MeCN,AlMe_2Cl}$. Several experiments were carried out. In a typical one, the adduct (14·4 g., 106 mmoles) was heated under nitrogen to about 160°, evolution of methane then starting at first slowly, but soon so rapidly that about 2·5 l. of methane were evolved during one minute. The product was then heated under vacuum. At about 80—100° a colourless liquid (1 g.) distilled off, and at about 150° a colourless waxy sublimate (0·25 g.) collected in the cool part of the apparatus, leaving the bulk of the reaction mixture as an involatile residue.

The liquid, purified by vacuum distillation at 80°, was identified as *isopropylideneaminomethylaluminium chloride dimer* $(\mathrm{Me_2C{:}N{\cdot}AlMeCl})_2$ (Found: Al, 20·9; hydrolysable methyl, 11·6%; *M*, 299. $\mathrm{C_8H_{18}Al_2Cl_2N_2}$ requires Al, 20·2; hydrolysable methyl, 11·3%; *M*, 267); $\nu_{\text{max.}}$ (liquid film) 3300w, 2933s, 2890m, 2849wsh, 2825wsh, 1650vs, 1433m, 1368s, 1239s, 1192vs, 1076wsh, 1060wm, 973w, 877m, 845ms, 737ssh, 699vs, 566m, 489wm, and 454m(br) cm.$^{-1}$. Hydrolysis gave methane and a solution in which acetone, ammonia, chloride and aluminium could be detected.

The waxy solid was identified as an isomer of the liquid (Found: Al, 19·8; hydrolysable methyl, 11·4%). It was too insoluble in benzene for determination of *M*, and the quality of the infrared spectrum obtained was poor; in the region 1600—1700 cm.$^{-1}$ there were two peaks, at 1695s and 1640m cm.$^{-1}$. Hydrolysis gave methane and a solution containing acetone, ammonia, chloride, and aluminium.

The involatile residue was insoluble in the common organic solvents. Its infrared spectrum had broad bands around 2300 and 1650 cm.$^{-1}$. Hydrolysis gave methane and a solution containing aluminium, chloride and acetone.

(*e*) *Dimethylaluminium hydride.* Methyl cyanide (0·5 g., 12 mmoles) was condensed at −196° on to a frozen solution of dimethylaluminium hydride (0·5 g., 9 mmoles) in methylcyclohexane (5 c.c.). The mixture was allowed to warm and the reaction which occurred as the mixture melted raised the temperature of the vessel to 50—60°. Methylcyclohexane and unchanged methyl cyanide were pumped off leaving a colourless liquid, identified as *ethylideneaminodimethylaluminium dimer*, $(\mathrm{MeCH{:}N{\cdot}AlMe_2})_2$ (Found: Al, 26·4; hydrolysable methyl, 30·0%; *M*, 220. $\mathrm{C_8H_{20}Al_2N_2}$ requires Al, 27·2; hydrolysable methyl, 30·3%; *M*, 198); $\nu_{\text{max.}}$ (liquid film) 2915s, 2882m, 2825wsh, 1675vs, 1639m, 1429m, 1397w, 1361m, 1190vs, 1124m, 785m, 715sh, 690vs, 560w, and 465w cm.$^{-1}$. The compound slowly turned yellow when left under nitrogen at 20°, and gave a pale yellow glass when distilled under vacuum at 70—80°. It decomposed very rapidly when exposed to air, and was hydrolysed by dilute acids to acetaldehyde, methane, and ammonium and aluminium salts.

The action of an excess of dimethylaluminium hydride (1·137 g., 19·6 mmoles) in 30 c.c. hexane on methyl cyanide (0·402 g., 9·8 mmoles) was also studied. The reactants were mixed at room temperature. The heat of reaction caused the solvent to boil, and the mixture was subsequently kept at this temperature for 15 min. The hexane was then removed under vacuum, leaving an involatile viscous oil, which had bands at ~1770 and 1640 cm.$^{-1}$ in the infrared spectrum, indicating that reaction was incomplete. After being heated at 145° for a further 30 min., the residual glue was hydrolysed with strong sodium hydroxide solution to give methane and ethylamine together with some hydrogen and ammonia.

Reaction of Ethyl Cyanide with Trimethylaluminium.—The *adduct* $\mathrm{EtCN,AlMe_3}$, m. p. 30°, was prepared by the action of an excess of ethyl cyanide on trimethylaluminium, the excess being removed by evacuation, and purified by vacuum distillation at about 70° (Found: Al, 20·9; hydrolysable methyl, 35·5%; *M*, 136. $\mathrm{C_6H_{14}AlN}$ requires Al, 21·3; hydrolysable methyl, 35·5%; *M*, 127).

Thermal decomposition of $\mathrm{EtCN,AlMe_3}$. A sample of adduct (1·695 g., 13·3 mmoles), when heated at 170° for 1 hr. in a sealed tube, formed methane (5·1 mmoles) and *dimethyl-s-butylideneaminoaluminium dimer* $(\mathrm{EtCMe{:}N{\cdot}AlMe_2})_2$ (0·44 g., 1·7 mmoles), isolated as colourless crystals, m. p. 73°, by vacuum sublimation at 60° from the red-brown reaction mixture (Found: Al, 21·4; hydrolysable methyl, 23·4%; *M*, 261. $\mathrm{C_{12}H_{28}Al_2N_2}$ requires Al, 21·3; hydrolysable methyl, 23·6%; *M*, 254); $\nu_{\text{max.}}$ (KBr disc) 2967m, 2924s, 2882wsh, 1653vs, 1456m, 1427w, 1364m, 1309vw, 1264m, 1212m, 1181s, 1103m, 1075w, 1017vw, 965wsh, 951w, 789s, 710s sh, 682vs, 550w, and 465w cm.$^{-1}$. Hydrolysis of this compound with dilute acid resulted in the evolution of methane; ethyl methyl ketone was detected in the resulting solution.

The red-brown glassy residue, when hydrolysed with 2N-sulphuric acid, gave methane and a solution containing aluminium, ammonia, and ethyl methyl ketone (Found: Al, 20·7; hydrolysable methyl, 20·1%. Me : Al ratio 1·8). Although the infrared spectrum of the residue contained a broad weak band at about 2300 cm.$^{-1}$ apparently indicative of C≡N groups, no ethyl cyanide or propionic acid was detected among the products of acid or alkaline hydrolysis.

Reactions of t-Butyl Cyanide.—(*a*) *Trimethylaluminium.* The *adduct* $\mathrm{Bu^tCN,AlMe_3}$, m. p. 61°, was conveniently prepared by treating t-butyl cyanide with an excess of trimethylaluminium at −78°, allowing the mixture to warm to room temperature, and pumping off the residual trimethylaluminium. It was purified by vacuum sublimation at 55—60° (Found:

Al, 17·1; hydrolysable methyl, 29·2%; *M*, 165. $C_8H_{18}AlN$ requires Al, 17·4; hydrolysable methyl, 29·0%; *M*, 155); $\nu_{max.}$ (benzene solution, 450—200 cm.$^{-1}$) 412m, 262s, and 240s cm.$^{-1}$.

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

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

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

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

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

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

Thermal decomposition of $Bu^tCN,AlMe_2Cl$. Little decomposition of the adduct was detected at temperatures below 220°, but complete rearrangement occurred during 6 hr. at 240°, and a colourless, very air-sensitive solid could be vacuum-sublimed from the reaction mixture at 145°. This was identified as $(Bu^tCMe{:}N{\cdot}AlMeCl)_2$, m. p. 130° (Found: Al, 14·9; hydrolysable methyl, 8·4%; *M*, 365. $C_{14}H_{30}Al_2Cl_2N_2$ requires Al, 14·9; hydrolysable methyl, 8·6%; *M*, 351); $\nu_{max.}$ (CCl_4 solution) 2967s, 2874sh, 1625vs, 1473m, 1422w, 1372s, 1273w, 1261m, 1203s, 1147s, 1068m, 1045m, 981w, 942w, 871s, 861sh, 691s, 671s, 568w, 534m, 494sh, and 467m cm.$^{-1}$; (benzene solution) 439s, 405s, 382sh, and 315m(br) cm.$^{-1}$. After the sublimation, about half the reaction mixture remained as an involatile yellow glue.

(*e*) *Dimethylaluminium hydride.* A solution of dimethylaluminium hydride (10 mmoles) in hexane (15 c.c.) was added by syringe to t-butyl cyanide (0·83 g., 10 mmoles) at room temperature. A vigorous exothermic reaction occurred. Removal of the solvent afforded crystals of *dimethylneopentylideneaminoaluminium dimer*, $(Bu^tCH{:}N{\cdot}AlMe_2)_2$, m. p. 89°, purified by vacuum distillation–sublimation at 110° (Found: Al, 19·0; hydrolysable methyl, 20·9%; *M*, 275. $C_{14}H_{32}Al_2N_2$ requires Al, 19·1; hydrolysable methyl, 21·3%; *M*, 282); $\nu_{max.}$ (Nujol mull) 1661vs, 1412s, 1274w, 1192vs, 1035s, 946m, 924m, 898s, 779vs, 689vs (br)580s, and 507m cm.$^{-1}$; (benzene solution) 449s, 380vs, 345w, 306sh, and 297s cm.$^{-1}$.

Reaction between Hydrogen Cyanide and Dimethylaluminium Hydride.—When dimethylaluminium hydride (0·311 g., 5·4 mmoles) in hexane (8 c.c.) was treated with hydrogen cyanide (120 N-c.c., 5·4 mmoles) at −78°, hydrogen (121 N-c.c., 5·4 mmoles) was evolved and dimethylaluminium cyanide $(Me_2AlCN)_4$, m. p. 89°, was isolated from the mixture and identified by its infrared spectrum.[19]

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