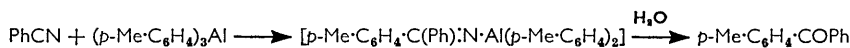


483. Reactions of Organoaluminium Compounds with Cyanides. Part I. Phenyl Cyanide

By J. E. LLOYD and K. WADE

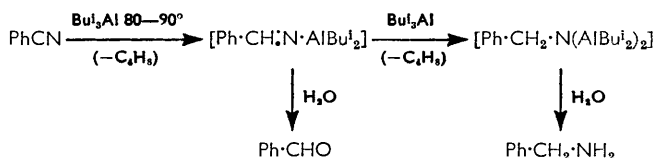
Phenyl cyanide reacts with Me_3Al , Et_3Al , Ph_3Al , and Me_2AlCl to form 1 : 1 adducts which rearrange at 130—200° to form the benzylideneamino-derivatives $(\text{PhMeC}:\text{N}\cdot\text{AlMe}_2)_2$, $(\text{PhCH}:\text{N}\cdot\text{AlEt}_2)_2$, $(\text{Ph}_2\text{C}:\text{N}\cdot\text{AlPh}_2)_n$, and $(\text{PhMeC}:\text{N}\cdot\text{AlMeCl})_2$, respectively. Phenyl cyanide and Me_2AlH react directly at 20° to form $(\text{PhCH}:\text{N}\cdot\text{AlMe}_2)_2$. Features of the infrared spectra of these air- and moisture-sensitive compounds are discussed. The proton magnetic resonance spectra of the benzylideneamino-derivatives support a nitrogen-bridged structure for the dimers, with *cis*- and *trans*-isomers present in the case of $(\text{PhMeC}:\text{N}\cdot\text{AlMe}_2)_2$.

REACTIONS between nitriles and organoaluminium compounds have been studied by several groups of workers, who have shown that ketones, aldehydes, or amines may be obtained by hydrolysis of the reaction mixture, although the aluminium-containing intermediates have been little studied. For example, Gilman and Marple¹ obtained phenyl *p*-tolyl ketone in 17% yield from phenyl cyanide and tri-*p*-tolylaluminium at about 130—140°:



Acetophenone has been prepared in 26—39% yield from phenyl cyanide using methylaluminium dichloride at 170°, and in 48—60% yield using dimethylaluminium chloride.²

The higher alkyls of aluminium tend to lose olefin when heated with nitriles; subsequent transfer of *hydrogen* affords an aldehyde or amine on hydrolysis:³



Dibutylaluminium hydride itself, Bu_2AlH , reacts similarly.³⁻⁵ Vacuum distillation of a mixture of propyl cyanide and Bu_2AlH was reported to give *n*-butylideneaminodibutylaluminium, $(\text{Pr}\cdot\text{CH}:\text{N}\cdot\text{AlBu}_2)_n$, the molecular weight of which was not recorded.⁴

Although nitriles are reduced to amines by an excess of lithium aluminium hydride⁶ the reduction can be stopped at the C=N stage by limiting the amount of LiAlH_4 ,⁷ or by use of the ethoxy-derivative $\text{LiAlH}(\text{OEt})_3$.⁸ The intermediates considered to be involved in such reductions have been discussed recently,⁸ but these have not been isolated and characterised, although polyiminoalanes $(\text{EtNAlH})_n$, from MeCN and $\text{R}_3\text{N}\cdot\text{AlH}_3$, have been described.⁹

Further work on the phenyl cyanide-triphenylaluminium system has shown that a crystalline solid adduct, $\text{PhCN}\cdot\text{AlPh}_3$, can be prepared by direct reaction of the components in benzene solution.¹⁰ This rearranges slowly at 90° and more rapidly at 140°

¹ H. Gilman and K. E. Marple, *Rec. Trav. chim.*, 1936, **55**, 133.

² S. Pasykiewicz, W. Dahlig, and B. Tomaszewski, *Roczniki Chem.*, 1962, **36**, 1383; see also H. Reinheckel and D. Jahnke, *Chem. Ber.*, 1964, **97**, 2661.

³ K. Ziegler, K. Schneider, and J. Schneider, *Annalen*, 1959, **623**, 9.

⁴ L. I. Zakharkin and I. M. Khorlina, *Doklady Akad. Nauk S.S.S.R.*, 1957, **116**, 422.

⁵ A. E. G. Miller, J. W. Biss, and L. H. Schwartzman, *J. Org. Chem.*, 1959, **24**, 627.

⁶ R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3738; L. H. Amundsen and L. S. Nelson, *ibid.*, 1951, **73**, 242; I. M. Soffer and M. Katz, *ibid.*, 1956, **78**, 1705.

⁷ H. C. Brown and C. J. Shoaf, *J. Amer. Chem. Soc.*, 1964, **86**, 1079.

⁸ H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1964, **86**, 1085.

⁹ R. Ehrlich, A. R. Young, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, 1964, **3**, 628.

¹⁰ T. Mole, *Austral. J. Chem.*, 1963, **16**, 801.

to form $(\text{Ph}_2\text{C}:\text{N}\cdot\text{AlPh}_2)_n$, m. p. 298–300°, for which ebullioscopic measurements on benzene solutions indicate a degree of association $n = 1.1\text{--}1.2$.¹¹

The present study was undertaken to obtain information on adducts $\text{RCN}\cdot\text{AlR}'_3$, their products of rearrangement, $(\text{RR}'\text{C}:\text{N}\cdot\text{AlR}'_2)_n$, and related compounds. Studies on phenyl cyanide are reported here; studies on alkyl cyanides will be reported later.

The organoaluminium compounds chosen as acceptor molecules were Me_3Al , Et_3Al , Ph_3Al , Me_2AlCl , and Me_2AlH . All react exothermally with phenyl cyanide at room temperature, the first four forming adducts $\text{PhC}:\text{N}\cdot\text{AlR}_3$ or $\text{PhC}:\text{N}\cdot\text{AlMe}_2\text{Cl}$, which rearrange further when heated, as described below. The hydride Me_2AlH forms $(\text{PhCH}:\text{N}\cdot\text{AlMe}_2)_2$ directly, no adduct $\text{PhC}:\text{N}\cdot\text{AlMe}_2\text{H}$ being isolable at room temperature.

Phenyl Cyanide Adducts.—The extremely air- and moisture-sensitive adducts $\text{PhC}:\text{N}\cdot\text{AlR}_3$ ($\text{R} = \text{Me}$, Et , or Ph) and $\text{PhC}:\text{N}\cdot\text{AlMe}_2\text{Cl}$ were characterised by hydrolysis or acid cleavage to determine groups R bound to aluminium, and by determination of aluminium and in one case nitrogen and chlorine by standard methods. Hydrolysis regenerated phenyl cyanide. Cryoscopic molecular-weight measurements using benzene solutions supported monomeric structures, and their infrared spectra showed bands in the region 2265–2273 cm^{-1} characteristic of co-ordinated $\text{C}\equiv\text{N}$ groups, $\nu(\text{C}\equiv\text{N})$ being raised some 35–43 cm^{-1} relative to that of the free nitrile, as shown in Table I. The increase ($\Delta\nu$ in Table I) in the frequency associated with the $\text{C}:\text{N}$ stretching vibration on co-ordination is a familiar feature of the spectra of nitrile adducts. It has generally been attributed^{12,13} to the mechanical constraint imposed on the vibration of the nitrogen in the linear adducts compared with the free nitrile, although an actual strengthening of the $\text{C}:\text{N}$ bond on co-ordination has also been suggested.¹⁴ Both explanations require $\Delta\nu$ to increase with the strength of the co-ordinate link, and the sequence indicated in Table I implies the order of increasing acceptor power to be $\text{AlPh}_3 < \text{AlEt}_3 < \text{AlMe}_3 = \text{AlMe}_2\text{Cl} < \text{BCl}_3$

TABLE I
Infrared spectroscopic data for adducts, $\text{PhCN}\cdot\text{AlR}_3$

Compound	State	$\nu(\text{C}:\text{N})$ (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\nu(\text{Al-N})$ (cm^{-1})
PhCN	Liquid	2230	—	—
$\text{PhCN}\cdot\text{AlPh}_3$	Nujol mull	2265	35	411
$\text{PhCN}\cdot\text{AlEt}_3$	Liquid	2270	40	394
$\text{PhCN}\cdot\text{AlMe}_3$	Nujol mull	2273	43	391
$\text{PhCN}\cdot\text{AlMe}_2\text{Cl}$	Benzene solution	2273	43	412
$\text{PhCN}\cdot\text{BCl}_3$	Benzene solution ¹²	2317	87	—

(figures for BCl_3 are taken from ref. 14 for comparison), a sequence in approximate agreement with the relative electronegativities of the groups attached to aluminium. However, recent calculations by Beattie and Gilson¹⁵ of $\text{C}\equiv\text{N}$ and B-N stretching frequencies for adducts $\text{MeCN}\cdot\text{BX}_3$ ($\text{X} = \text{F}$, Cl , or Br) have shown the need for caution in relating $\Delta\nu$ to Lewis acidity in nitrile adducts. As the overall variation in $\Delta\nu$ for the organoaluminium compounds is only 8 cm^{-1} , and individual values are accurate only to ± 2 cm^{-1} , it is not possible to draw detailed conclusions from these figures.

If this sequence reflects increasingly strong Al-N bonding, the frequency of the absorption associated with the Al-N stretching vibration might be expected to follow a similar sequence. Assignment of the correct band in the spectrum to this vibration is, however, less certain than in the case of $\nu(\text{C}\equiv\text{N})$. Greenwood and co-workers¹⁶ have identified a band at 533 cm^{-1} with the Al-N stretching vibration in the spectrum of $\text{Me}_3\text{N}\cdot\text{AlH}_3$, and bands at 460 and 461 cm^{-1} in the spectrum of $(\text{Me}_3\text{N})_2\text{AlH}_3$, whilst Beachley, Coates, and

¹¹ G. K. J. Gibson and D. W. Hughes, *Chem. and Ind.*, 1964, 544.

¹² H. J. Coerver and C. Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

¹³ T. L. Brown and M. Kubota, *J. Amer. Chem. Soc.*, 1961, **83**, 4175; D. Cook, *Canad. J. Chem.*, 1962, **40**, 480.

¹⁴ W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J.*, 1960, 2182.

¹⁵ I. R. Beattie and T. Gilson, *J.*, 1964, 2292.

¹⁶ G. W. Fraser, N. N. Greenwood, and B. P. Straughan, *J.*, 1963, 3742.

Kohnstam¹⁷ found the corresponding bands in the spectra of $(\text{Me}_2\text{NAlMe}_2)_2$ and $[(\text{CD}_3)_2\text{NAlMe}_2]_2$ at 508 and 482 cm^{-1} , respectively. As nitriles are weaker donors than amines, the Al-N stretching vibration in a phenyl cyanide adduct might be expected to give rise to a band in the region 400—500 cm^{-1} . The spectra of the adducts in the region 250—500 cm^{-1} were recorded, and all contained a band between 440 and 500 cm^{-1} , another rather sharper band between 391 and 412 cm^{-1} , and at least one other broader and generally weaker band at a lower frequency. The band near 400 cm^{-1} (listed in Table 1) is considered to be that associated with an Al-N stretching vibration, as a band between 401 and 412 cm^{-1} , but not between 440 and 500 cm^{-1} , is also present in the spectra of methyl cyanide adducts analogous to those discussed here,¹⁸ and a band between 440 and 500 cm^{-1} would be expected in the spectra of phenyl compounds, being associated with an out-of-plane bending vibration (ν_{19} in Herzberg's nomenclature¹⁹). The spectrum of $\text{PhCN}\cdot\text{AlPh}_3$ is clearly complicated by further bands associated with the aluminium-substituted benzene rings (cf., for example, the spectra of phenyl derivatives of silicon, germanium, tin, and lead in this region²⁰), and that of $\text{PhCN}\cdot\text{AlMe}_2\text{Cl}$ by Al-Cl modes.²¹ If our assignment of $\nu(\text{Al-N})$ is correct, the values for the individual adducts indicate no great variation in the strength of the Al-N bond from one adduct to another, and the same relation of frequency to acceptor strength as found for $\nu(\text{CN})$ is not observed.*

Rearrangement Reactions.—These are summarised in Table 2. It is apparent that migration of hydrogen from aluminium to the carbon of the cyanide group occurs at a temperature some 150° below that at which organic groups readily undergo a similar migration. Since experimental procedures varied, the slightly different reaction temperatures found convenient for the rearrangements involving migration of methyl and phenyl

TABLE 2
Thermal rearrangement of adducts, $\text{PhCN}\cdot\text{AlR}_3$

Adduct	M. p.	Temp.	Reaction ^a	Product	M. p.	Yield (%)
$\text{PhCN}\cdot\text{AlMe}_3$	80°	160—170°	Me→	$(\text{PhCMe}\cdot\text{N}\cdot\text{AlMe}_2)_2$	109—114°	60
$\text{PhCN}\cdot\text{AlEt}_3$	Liqd.	190—200	C_2H_5 , ↑ H→	$(\text{PhCH}\cdot\text{N}\cdot\text{AlEt}_2)_2$	Liqd.	75
$\text{PhCN}\cdot\text{AlPh}_3$	Decomp.	130—150	Ph→	$(\text{Ph}_2\text{C}\cdot\text{N}\cdot\text{AlPh}_2)_n$	295—298	15
$\text{PhCN}\cdot\text{AlMe}_2\text{Cl}$...	83	170—180	Me→	$(\text{PhCMe}\cdot\text{N}\cdot\text{AlMeCl})_2$	135	60
$\text{PhCN}\cdot\text{AlMe}_2\text{H}^b$	—	<20	H→	$(\text{PhCH}\cdot\text{N}\cdot\text{AlMe}_2)_2$	143	90

* In this column, ↑ indicates gas evolved, → indicates group or atom migrating. ^b Adduct itself not isolated; 1 : 1 mixture of components used.

groups are not considered to reflect the relative migratory aptitudes of Me and Ph. The low yield of $(\text{Ph}_2\text{C}\cdot\text{N}\cdot\text{AlPh}_2)_n$, which refers to the pure product, probably reflects extensive decomposition at the temperature of its vacuum sublimation (240—250°, at which temperature Ph_3Al itself loses benzene). Experiments with $\text{PhCN}\cdot\text{AlEt}_3$ indicated that some migration of ethyl groups may occur at about 160°, although concurrent loss of ethylene and hydrogen migration led to mixed products which were difficult to separate. At 190—

* [Note Added in Proof.—I. R. Beattie and T. Gilson (*J.*, 1964, 3528) have recently shown that, in the spectrum of $(\text{Me}_3\text{N})_2\text{AlH}_3$, a band near 200 cm^{-1} is more properly designated $\nu(\text{Al-N})$, the band at 460 cm^{-1} being mainly associated with deformation of the trimethylamine groups. In the spectrum of $(\text{Me}_2\text{N})_2\text{AlMe}_2$, the sensitivity of the band near 500 cm^{-1} to deuteration of the dimethylamino-group¹⁷ shows that this band is also associated with a vibration involving more than just the aluminium and nitrogen atoms. For our adducts $\text{PhCN}\cdot\text{AlR}_3$ the extent to which Al-N stretching vibrations contribute to the band near 400 cm^{-1} must also be expected to be limited, and the lack of correlation between the frequency of this band and the acceptor strength of the organoaluminium hydride is therefore readily understood.]

¹⁷ O. T. Beachley, G. E. Coates, and G. Kohnstam, *J.*, 1965, in the press; O. T. Beachley and G. E. Coates, *J.*, 1965, in the press.

¹⁸ J. E. Lloyd and K. Wade, unpublished observations.

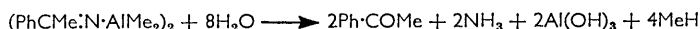
¹⁹ G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, pp. 118, 362—369; D. H. Whiffen, *J.*, 1956, 1350.

²⁰ L. A. Harrah, M. T. Ryan, and C. Tamborski, *Spectrochim. Acta*, 1962, 18, 21; A. L. Smith, *ibid.*, 1963, 19, 849.

²¹ A. P. Gray, *Canad. J. Chem.*, 1963, 41, 1511.

200°, the reaction involving loss of ethylene and hydrogen migration predominates, giving rise to a sudden evolution of gas, and allowing easy isolation of benzylideneaminodiethylaluminium, $(\text{PhCH:N}\cdot\text{AlEt}_2)_2$, in good yield. In this reaction triethylaluminium is acting effectively as a source of diethylaluminium hydride, in the same way that tri-isobutylaluminium, losing isobutene, acts as a source of di-isobutylaluminium hydride in its reactions with nitriles.³ At the temperatures used in the present work, however, there was no evidence of loss of a second mole of ethylene to form $(\text{PhCH}_2\text{N}\cdot\text{AlEt})_n$.

The *rearranged compounds*, the benzylideneamino-derivatives $(\text{PhCMe:N}\cdot\text{AlMe}_2)_2$, $(\text{PhCH:N}\cdot\text{AlEt}_2)_2$, $(\text{Ph}_2\text{C:N}\cdot\text{AlPh}_2)_n$, $(\text{PhCMe:N}\cdot\text{AlMeCl})_2$, and $(\text{PhCH:N}\cdot\text{AlMe}_2)_2$ were purified by vacuum sublimation or distillation and characterised as follows. Less sensitive to air and moisture than the parent adducts, they were nevertheless readily hydrolysed to the corresponding carbonyl compound, ammonia, aluminium hydroxide, and hydrocarbon, e.g.,



The chloro-compound also gave hydrogen chloride. Measurement of the hydrocarbon formed showed that migration of one organic group from aluminium had occurred, and the aluminium content confirmed the formula. Nitrogen and chlorine analyses were also carried out on the chloro-compound. Cryoscopic molecular-weight measurements using benzene solutions supported dimeric structures for those compounds which were soluble. The insoluble phenyl compound, $(\text{Ph}_2\text{C:N}\cdot\text{AlPh}_2)_n$, has been found by Gibson and Hughes¹¹ to be monomeric in boiling benzene.

The infrared spectra of the rearranged compounds showed strong bands attributable to the C:N stretching vibration as follows: $(\text{PhCH:N}\cdot\text{AlMe}_2)_2$, 1630 cm^{-1} ; $(\text{PhCH:N}\cdot\text{AlEt}_2)_2$, 1633 cm^{-1} ; $(\text{PhCMe:N}\cdot\text{AlMe}_2)_2$, 1634 cm^{-1} ; $(\text{PhCMe:N}\cdot\text{AlMeCl})_2$, 1613 cm^{-1} . These bands are close to the region ($\sim 1640 \text{ cm}^{-1}$) in which similar bands are found for related boron compounds $(\text{RCH:N}\cdot\text{BHBu}^t)_2$ (R = aryl).²² Two factors are probably contributing to lower the frequency slightly, relative to that generally associated with C=N stretching vibrations.²³ Conjugation of C=N with a phenyl group lowers the frequency relative to that observed for analogous alkyl compounds^{18, 22, 24} (1650—1690 cm^{-1}) and the dimeric structures such as (I) involve donor links from the nitrogen atoms of the benzylidene-amino-groups which will tend to reduce the C=N bond order.

Assignment of the C=N stretching band in the spectrum of $(\text{Ph}_2\text{C:N}\cdot\text{AlPh}_2)_n$ is less certain. There is no intense band in the region in which these bands occur in the spectra of the other four compounds, but slight inflexions at 1660 and 1620 cm^{-1} on the side of a very strong band at 1595 cm^{-1} . A band associated with a C—C stretching vibration of a benzene ring would be expected at this last frequency and is in fact observed, although with weaker intensity, in the spectrum of the adduct $\text{PhCN}\cdot\text{AlPh}_3$. It seems unlikely that $\nu(\text{C}=\text{N})$ is at such a low frequency as to coincide with this band, although *two* phenyl groups are now conjugated with the C=N bond. Gibson and Hughes¹¹ assign the small inflexion at 1660 cm^{-1} to the C=N stretching vibration, although the less well-defined inflexion at 1620 cm^{-1} seems more likely by comparison with our other compounds.

Bands associated with Al—N vibrations have not been identified in the spectra of the rearranged compounds. The related compound $(\text{Me}_2\text{N}\cdot\text{AlMe}_2)_2$ ¹⁷ has $\nu(\text{Al-N})$ 508 cm^{-1} . The spectra of all our rearranged compounds have a band in the region 443—481 cm^{-1} , which may be associated with Al—N vibrations, but as the benzene ring vibration, ν_{19} , should also give rise to a band in this region,^{19, 20} unambiguous assignment has not been possible. Studies on related alkyl compounds may resolve this uncertainty.

The rearranged compounds described here are the first examples of alkyl- or arylideneaminoaluminium compounds in which the 3-co-ordinate nitrogen atoms are present

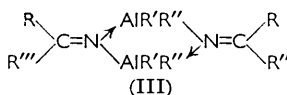
²² M. F. Hawthorne, *Tetrahedron*, 1962, **17**, 117.

²³ L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 226.

²⁴ J. E. Lloyd and K. Wade, *J.*, 1964, 1649.

in a four-membered (Al-N)₂ ring, in which the bond-angle strain (distortion from 120° to about 90°) at the nitrogen atoms appears to be greater than in the related amino-alanes (R₂N·AIR'₂)₂ (distortion from 109 to 90°). A trimeric form (R₂C:N·AIR'₂)₃ which would have no distortion of the bond angles, has not been detected in any of the systems at present studied. The apparently important effect which the mode of formation has on the state of association of amino-alanes and related compounds has been discussed recently by Beachley and Coates.¹⁷ In the present examples, the rearrangement of the monomeric adducts could involve two molecules and lead directly to the dimer. An intramolecular rearrangement with subsequent dimerisation appears less likely.

The structures of the dimeric benzyldeneamino-alanes, (RR'''C:N·AIR'R'')₂ like the related ethylideneaminoboranes,²⁴ allow the possibility of *cis-trans*-isomerism in those cases where R and R''' are different, or where R' and R'' are different. In the situation in which R and R''' differ, it has been shown²⁴ that the proton magnetic resonance (p.m.r.) spectrum can be used to detect the presence of isomers, since in the *trans*-isomer [*e.g.*, (II)] the groups attached to aluminium will be magnetically equivalent, each having one group R and one R''' as near neighbours, whereas in the *cis*-isomer (III) these groups on aluminium are no longer equivalent, one set having groups R as near neighbours, the other set having R''' as neighbours.



The p.m.r. of those compounds which proved soluble enough in carbon tetrachloride to be studied have been recorded (Table 3).

TABLE 3
Proton magnetic resonance spectroscopic data (τ values) for carbon tetrachloride solutions

Compound	=C-Ph	=C-Mc	Al-Me or Al-Et
(PhMeC:N·AlMe ₂) ₂	2·5 ₇ c	7·5 ₁ s, 7·5 ₇ s	10·7 ₀ s, 10·9 ₆ s, 11·2 ₃ s
(PhCH:N·AlMe ₂) ₂	2·4 ₆ c	—	10·7 ₁ s
(PhCH:N·AlEt ₂) ₂	2·7c		9·0c, 10·0c

s = singlet, c = complex

Dimethyl-(α -methylbenzyldeneamino)aluminium (PhMeC:N·AlMe₂)₂.—*cis*- and *trans*-Isomers are possible, differing in the relative orientation of the groups PhMeC:, and the p.m.r. spectrum shows both to be present. The three peaks at highest field do not form a triplet and are best explained as a singlet at τ 10·9₆ due to the four equivalent *Al*-methyl groups in a *trans*-structure (II; R = Ph, R' = R'' = R''' = Me), and two smaller peaks of equal intensity at τ 10·7₀ and 11·2₃ arising from the two non-equivalent sets of *Al*-methyl groups in a *cis*-structure (III). The phenyl group gives rise to a broad peak at τ 2·5₇ and the C-methyl groups to two peaks at τ 7·5₁ and 7·5₇. These last are probably due to two slightly different chemical shifts in the two isomers.

Benzyldeneaminodimethylaluminium (PhCH:N·AlMe₂)₂.—No evidence was obtained for isomeric forms. The compound was not very soluble, so that the peaks were rather weak. A singlet at τ 10·7₁ is attributable to the *Al*-methyl groups, and that at τ 2·4₆ to the phenyl groups. The methine hydrogen peak was not visible, but would be expected to be a weak broad peak near the phenyl peak.

Benzyldeneaminodiethylaluminium (PhCH:N·AlEt₂)₂.—A complex peak at τ 2·7 can be assigned to the phenyl group. Complex peaks at τ 9·0 and 10·0 evidently arise from the CH₂ and CH₃ groups of the ethyl groups. The complexity of the spectrum, however, makes interpretation in terms of isomers impossible [cf. (MeCH:N·BEt₂)₂²⁴].

EXPERIMENTAL

Materials.—Phenyl cyanide was purified by distillation from phosphorus pentoxide. Technical grade trimethylaluminium and triethylaluminium were purified by vacuum distillation.

Triphenylaluminium-ether complex, m. p. 127—128°, from phenyl-lithium and aluminium chloride in ether,²⁵ was purified by recrystallisation from toluene. Dimethylaluminium hydride was obtained as a solution in methylcyclohexane from the reaction between trimethylaluminium and lithium aluminium hydride in methylcyclohexane in a sealed tube at 70°, the product and solvent being distilled from the reaction tube under vacuum.²⁶ Dimethylaluminium chloride was distilled from a mixture of methylaluminium sesquichloride and sodium chloride.

Analyses.—Hydrogen, methyl, or ethyl groups attached to aluminium were determined by treatment of weighed samples of the compounds with 2-methoxyethanol followed by dilute sulphuric acid and subsequent measurement in the vacuum line of the volume of hydrogen, methane, or ethane produced. Phenyl groups attached to aluminium were determined by measurement of the benzene formed when weighed samples were treated with dry hydrogen chloride at room temperature. The aluminium content of solutions resulting from the hydrolysis of weighed samples was determined by either the oxime²⁷ or EDTA²⁸ method. Nitrogen was determined by the Kjeldahl method. Chlorine was determined titrimetrically by a method involving the use of mercury(II) oxycyanide.²⁹

Manipulations were carried out using a conventional vacuum-line, nitrogen-filled glove boxes, or nitrogen-filled apparatus. Molecular weights were determined cryoscopically in benzene.

Infrared spectra (range 2—25 μ) were recorded on a Grubb-Parsons GS2A prism-grating spectrometer or Spectromaster; spectra in the range 21—50 μ were recorded on a Grubb-Parsons DB3/DM2 caesium iodide spectrometer. Samples were in the form of liquid films, Nujol mulls, solutions in carbon tetrachloride, or pressed potassium bromide discs as appropriate.

Nuclear magnetic resonance spectra were recorded at 60 Mc./sec. on an A.E.I. R.S.2 or a Perkin-Elmer spectrometer. Samples were dissolved in carbon tetrachloride with tetramethylsilane as the reference compound.

Reaction of Phenyl Cyanide with Trimethylaluminium.—The adduct $\text{PhCN}\cdot\text{AlMe}_3$, m. p. 80°, was prepared by direct reaction of equimolar proportions of phenyl cyanide and trimethylaluminium under nitrogen at room temperature, and purified by vacuum sublimation (Found: Al, 15.4; Me, 25.8%; *M*, 169. $\text{C}_{10}\text{H}_{20}\text{AlN}$ requires Al, 15.4; Me, 25.7%; *M*, 175), ν_{max} . (Nujol) 2273s cm^{-1} ($\text{C}\equiv\text{N}$). The product reacts vigorously with air and moisture.

Dimethyl-(α -methylbenzylideneamino)aluminium Dimer ($\text{PhCMe}_2\text{N}\cdot\text{AlMe}_2$)₂.—The foregoing adduct (3.83 g., 21.9 mmoles) was heated at 160—170° for 4 hr. under nitrogen, forming a yellow glass which on vacuum sublimation at 120° afforded a colourless solid, m. p. 109—114° (2.0 g.), identified as the dimer (Found: Al, 15.2; Me, 16.9%; *M*, 366. $\text{C}_{20}\text{H}_{40}\text{Al}_2\text{N}_2$ requires Al, 15.4; Me, 17.1%; *M*, 350), ν_{max} . 3280vw, 3090w, 3060w, 3030w, 2920ms, 2880m, 2820w, 1634vs, 1572m, 1493m, 1443m, 1435sh, 1383w, 1361m, 1307vw, 1289m, 1266s, 1179s, 1085w, 990mw, 760s, 718s, 675s, 588w, and 565w cm^{-1} . The compound was much less sensitive to air than the adduct, being slowly hydrolysed by moist air and water, but rapidly by dilute acid to give acetophenone, identified as its 2,4-dinitrophenylhydrazone.

Reaction of Phenyl Cyanide with Triphenylaluminium.—Phenyl cyanide (4.0 g., 39 mmoles) and triphenylaluminium-ether complex (10.0 g., 30 mmoles) were heated together in benzene (25 c.c.) at 60° for $\frac{1}{2}$ hr. The solvent, ether, and residual phenyl cyanide were removed *in vacuo* leaving a colourless crystalline solid which was recrystallised from methylcyclohexane and identified as the adduct $\text{PhCN}\cdot\text{AlPh}_3$ (Found: Al, 7.5; Ph, 63.0%; *M*, 375. Calc. for $\text{C}_{25}\text{H}_{20}\text{AlN}$: Al, 7.5; Ph, 63.9%; *M*, 361), ν_{max} . (Nujol and KBr disc) 2265 cm^{-1} ($\text{C}\equiv\text{N}$).

Diphenyl-(α -phenylbenzylideneamino)aluminium, $(\text{Ph}_2\text{C}_2\text{N}\cdot\text{AlPh}_2)_n$.—When a sample of the foregoing adduct, (3 g.) was heated at 240—250° in an evacuated tube, a colourless crystalline solid (0.45 g.) sublimed to the cooler part of the tube. This was identified as $(\text{Ph}_2\text{C}_2\text{N}\cdot\text{AlPh}_2)_n$, m. p. 295° (Found: Al, 7.6; Ph, 42.8. Calc. for $\text{C}_{25}\text{H}_{20}\text{AlN}$: Al, 7.5; Ph, 42.7%), ν_{max} . (KBr disc) 3049m, 2985m, 1658vw, 1613(sh), 1595s, 1567s, 1488m, 1479m, 1445s, 1416s, 1361s, 1316m, 1289m, 1266s, 1247m, 1190m, 1155m, 1089s, 1080s, 1024m, 1000m, 951s, 919m, 909s, 889m, 862w, 840w, 787s, 762m, 729s, 700vs, 680s, 620s, 561s, 481s, and 456w cm^{-1} . The compound

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²⁷ W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.*, 1932, **209**, 129; A. Vogel, "Quantitative Inorganic Analysis," Longmans, Green, London, 1948, p. 453.

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was too insoluble in benzene and nitrobenzene for cryoscopic molecular weight measurements to be carried out. When hydrolysed with dilute acid the compound gave benzophenone, identified as its 2,4-dinitrophenylhydrazone.

Reaction of Phenyl Cyanide with Triethylaluminium.—Phenyl cyanide (1.59 g., 15.5 mmoles) and triethylaluminium (1.8 g., 15.5 mmoles) were mixed at -78° , and allowed to warm to room temperature. The heat evolved during reaction warmed the mixture to $50-60^\circ$. The product, a very pale yellow liquid, was identified as the *adduct*, $\text{PhCN}\cdot\text{AlEt}_3$ (Found: Al, 12.0; Et, 38.6%; M , 210. $\text{C}_{13}\text{H}_{20}\text{AlN}$ requires Al, 12.4; Et, 40.1%; M , 217), ν_{max} . (thin film between KBr plates) 2270 cm^{-1} ($\text{C}\equiv\text{N}$).

Benzylideneaminodiethylaluminium Dimer ($\text{PhCH}\cdot\text{N}\cdot\text{AlEt}_2$)₂.—When a sample of the foregoing adduct (4.8 g., 22 mmoles) was heated under nitrogen on an oil-bath, (bath temp. $\sim 190^\circ$) there was a sudden rapid evolution of about 300 c.c. of gas which was identified by its infrared spectrum as ethylene. As a further 150 c.c. ethylene was collected during prolonged heating at $190-200^\circ$, the total amount evolved was about 450 c.c. (20 mmoles). The residue was a dark red glue from which a pale yellow viscous liquid could be distilled *in vacuo* (bath temp. $200-210^\circ$) giving the *dimer* (Found: Al, 13.8; Et, 30.4%; M , 420. $\text{C}_{22}\text{H}_{32}\text{Al}_2\text{N}_2$ requires Al, 14.3; Et, 30.7%; M , 378), ν_{max} . (liquid film) 3268w, 3050m, 3020m, 2925s, 2779m, 1690m, 1633vs, 1600s, 1582s, 1494m, 1456s, 1408s, 1373m, 1311s, 1282s, 1228s, 1203s, 1192m, 1177m, 1160w, 1102w, 1076m, 1053w, 1020w, 984s, 945s, 914s, 840s, 811w, 778s, 748s, 702vs, 676vs, 625vs, 540s, and 468m cm^{-1} . Hydrolysis with dilute acid gave benzaldehyde, identified as its 2,4-dinitrophenylhydrazone and phenylhydrazone.

Reaction of Phenyl Cyanide with Dimethylaluminium Chloride.—Phenyl cyanide (1.7 g., 16.5 mmoles) and dimethylaluminium chloride (1.5 g., 16.2 mmoles) reacted exothermically to give a colourless crystalline solid which could be vacuum sublimed at 120° to give the pure *adduct*, $\text{PhCN}\cdot\text{AlMe}_2\text{Cl}$, m. p. 83° (Found: Al, 13.7; Cl, 17.9; Me, 15.6%; M , 196. $\text{C}_9\text{H}_{11}\text{AlClN}$ requires Al, 13.8; Cl, 18.2; Me, 15.4%; M , 196), ν_{max} . (benzene solution) 2273 cm^{-1} ($\text{C}\equiv\text{N}$).

Methyl-(α -methylbenzylideneamino)aluminium Chloride Dimer, ($\text{PhCMe}\cdot\text{N}\cdot\text{AlMeCl}$)₂.—When the foregoing adduct was heated for 20 hr. at $170-180^\circ$, the product was a yellow-brown viscous liquid which set to a yellow glass at room temperature. A sample sublimed at 140° *in vacuo* giving a colourless solid, m. p. 135° , identified as the *dimer* (Found: Al, 13.8; Cl, 18.0; N, 7.0; Me, 6.4%; M , 397. $\text{C}_{18}\text{H}_{22}\text{Al}_2\text{Cl}_2\text{N}_2$ requires Al, 13.8; Cl, 18.1; N, 7.2; Me, 7.7%; M , 391), ν_{max} . (Nujol) 1619s, 1603(sh), 1572m, 1453m, 1296w, 1271m, 1188m, 1088w, 1025w, 995w, 922w, 764s, 722s, 669s, 635w, 529m, and 443m cm^{-1} . Dilute acid hydrolysis gave acetophenone, identified as its 2,4-dinitrophenylhydrazone. The compound decomposed slowly under nitrogen at room temperature, turning yellow in colour. Pure samples could not be recovered from the residue by vacuum sublimation.

Reaction of Phenyl Cyanide with Dimethylaluminium Hydride; Formation of Benzylideneaminodimethylaluminium Dimer, ($\text{PhCH}\cdot\text{N}\cdot\text{AlMe}_2$)₂.—Phenyl cyanide (1 g., 10 mmoles) and a solution of dimethylaluminium hydride ($\sim 0.5\text{ g}$., 9 mmoles) in methylcyclohexane (5 c.c.) were mixed at -196° and allowed to warm to room temperature. The heat of the reaction raised the temperature of the solution to about 50° ; on subsequent cooling, colourless crystals separated. The solvent was pumped off, and the residue was heated to 140° *in vacuo*, giving a colourless sublimate (1.3 g.), m. p. 143° , of the *dimer* (Found: Al, 16.4; Me, 18.6%; M , 329. $\text{C}_{18}\text{H}_{24}\text{Al}_2\text{N}_2$ requires Al, 16.8; Me, 18.6%; M , 322), ν_{max} . (Nujol) 1683w, 1630vs, 1595s, 1580s, 1496w, 1452s, 1411m, 1380w, 1333vw, 1313m, 1290m, 1203s, 1183vs, 1101vw, 1077m, 1023m, 1001w, 967m, 913w, 840vs, 745vs, 685vs, 615w, 575m, and 470w cm^{-1} . The compound was easily hydrolysed by water or dilute acid to form benzaldehyde, identified as its phenylhydrazone.

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