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INSERTION REACTIONS OF DIETHYLALUMINIUM DERIVATIVES
II. REACTION OF DIETHYLALUMINIUM DIMETHYLAMIDE AND DIETHYLALUMINIUM ETHANETHIOLATE WITH NITRILES

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SUMMARY

Diethylaluminium dimethylamide, Et_2AlNMe_2, has been found to react with equimolar amount of benzonitrile or *p*-substituted benzonitriles, XC_6H_4CN ($X=NO_2$, Me, OMe, NMe_2), to give diethylaluminium benzamidine derivatives, $Et_2Al-N{=}C(XC_6H_4)-NMe_2$. These products result from addition of the Al–N bond across the C≡N bond. The order of reactivity for *p*-substituted benzonitriles is $X=NO_2 > H \simeq CH_3 > OMe > NMe_2$, the reverse of the order of π-electron density on CN group, which suggests the initial step of the reaction is not the formation of a π-complex, but the formation of the complex, $RC{\equiv}N{\rightarrow}Al(NMe_2)Et_2$, which is followed by nucleophilic migration of the NMe_2 group to the C atom of the CN group.

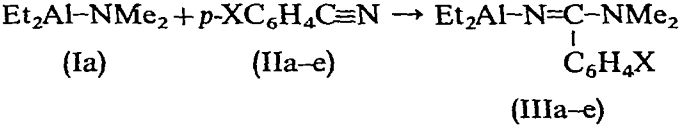
Acetonitrile and benzyl cyanide react similarly with Et_2AlNMe_2 to give crystalline addition products. Ethyl cyanoacetate reacts with evolution of an equivalent amount of ethane and formation of a solid.

Diethylaluminium ethanethiolate, Et_2AlSEt, which reacts readily with isocyanates, reacts also with many nitriles, but the usual addition products are difficult to isolate except in the case of acetonitrile.

INTRODUCTION

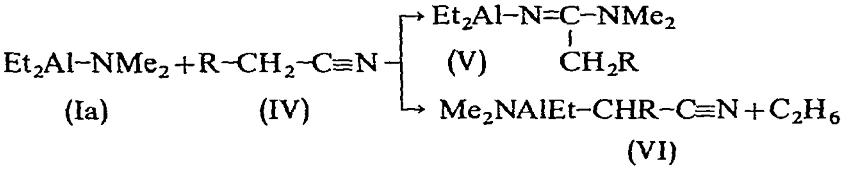
Studies on the reactions between nitriles and organoaluminium compounds, especially trialkylaluminium were carried out by Reinheckel *et al.*[1], Wade *et al.*[2] and Pasynkiewicz[3], and the occurrence of both alkylation and reduction reaction was reported. In our previous paper[4], diethylaluminium dimethylamide and ethanethiolate, Et_2AlX [$X=NMe_2$ (Ia), $X=SEt$ (Ib)], were shown to react with isocyanates to give 1/1 addition products and cyclic trimers of the isocyanates. We expected that (Ia) and (Ib) would react with nitrile compounds, which are known to be relatively weak acceptors[5], and began to examine the reactions between (Ia) or (Ib) and benzonitriles or acetonitriles. During our work, Hoberg and Mur[6] reported the analogous addition reaction of $Et_{2-n}(X)_nAlNEt_2$ compounds ($X=$halogen) with benzonitrile. The reaction product from trialkylaluminium and dimethylcyanamide is known to have the structure, $R'_2N-CR{=}N-AlR_2$[7].

We have now studied the reactions of diethylaluminium dimethylamide (Ia) with *p*-substituted benzonitriles or substituted acetonitriles, and the reaction of (Ib) with some of the nitriles. Reactions between (Ia) and *p*-substituted benzonitriles, *p*-XC_6H_4CN [X = H (IIa), Me (IIb), NO_2 (IIc), MeO (IId) and Me_2N (IIe)] occurred at 80° for 20 h and gave crystalline 1/1 addition products (IIIa)–(IIIe) at different rates (eqn. 1). When the rates were qualitatively compared, the *p*-substituents were found to affect markedly the reactivity of (II), the more electronegative group giving the higher rate.



$$\underset{\text{(Ia)}}{Et_2Al\text{-}NMe_2} + \underset{\text{(IIa–e)}}{p\text{-}XC_6H_4C{\equiv}N} \rightarrow \underset{\text{(IIIa–e)}}{Et_2Al\text{-}N{=}\underset{C_6H_4X}{\underset{|}{C}}\text{-}NMe_2} \qquad (1)$$

In the case of the acetonitrile derivatives (IV), which contain α-hydrogen atoms. there should be two competing reactions; (1) nucleophilic attack of the NMe_2 group in (Ia) on the C-atom of the C≡N bond of (IV) to give the products (V), and (2), elimination of α-hydrogen atom with ethane evolution to give the products (VI) [see eqn. (2)].



$$\underset{\text{(Ia)}}{Et_2Al\text{-}NMe_2} + \underset{\text{(IV)}}{R\text{-}CH_2\text{-}C{\equiv}N} \left\{ \begin{array}{l} \rightarrow \underset{\text{(V)}}{Et_2Al\text{-}N{=}\underset{CH_2R}{\underset{|}{C}}\text{-}NMe_2} \\ \rightarrow \underset{\text{(VI)}}{Me_2NAlEt\text{-}CHR\text{-}C{\equiv}N + C_2H_6} \end{array} \right. \qquad (2)$$

Acetonitrile (IVa) (R = H) and benzyl cyanide (IVb) (R = C_6H_5) gave the products (Va) and (Vb), respectively. Ethyl cyanoacetate (IVc) (R = CO_2Et) reacted differently to give (VIc) and ethane. Diethylaluminium ethanethiolate (Ib) reacted with nitriles with coloration due to complex formation, but the addition products could not be isolated and except for acetonitrile the starting materials were recovered by distillation.

$$\underset{\text{(Ib)}}{Et_2Al\text{-}SEt} + \underset{\text{(II) or (IV)}}{R\text{-}C{\equiv}N} \rightarrow \underset{\text{(VII) (R = Me)}}{Et_2Al\text{-}N{=}CR\text{-}SEt} \qquad (3)$$

EXPERIMENTAL

General remarks

Et_2AlNMe_2 (Ia) and Et_2AlSEt (Ib) were prepared according to our previous paper[4]. Benzonitrile, *p*-tolunitrile and three acetonitrile derivatives were purified by distillation of commercial reagents. *p*-Nitro-[8], *p*-methoxy-[9] and *p*-dimethylamino[10]-benzonitriles were synthesized by decomposition of the corresponding benzaldoximes. Hydrocarbon solvents were thoroughly dried over sodium wire. All the reactions and measurements of physical constants of the products were carried out under dry nitrogen or argon.

Measurement of physical constants

Molecular weights in benzene solution were determined cryoscopically. IR spectra in benzene solution on KCl were obtained using a Japan Spectroscopic Co.

model DS-403G spectrometer. NMR spectra were recorded on a Japan Electron Optics C-60 spectrometer 60 MHz using TMS as internal standard.

Reaction of Et_2AlNMe_2 (Ia) with benzonitrile (IIa)

(Ia) (5.9 mmoles) in 3 ml benzene was frozen at −78°, and an equimolar amount of (IIa) was added at once with a syringe. The mixture was shaken to give a homogeneous solution, and gradually warmed to room temperature. The reaction tube was stoppered tightly and placed in an oil bath at 80°. An absorption at 2240 cm^{-1} [$\nu(C{\equiv}N)$] in the IR spectrum of the mixture disappeared after 6 h and a crystalline product was precipitated by cooling the mixture at room temperature for one day. Removal of the solvent under reduced pressure, and recrystallization of the residue from hexane gave white needle-like (IIIa), m.p. 147–149°, in 75% yield. (IIIa) [$Et_2Al{-}N{=}C(C_6H_5){-}NMe_2$] was identified by IR and NMR spectra (in Tables 1, 2), and by elementary analysis. (Found: C, 67.09; H, 9.02; Al, 11.40; active ethyl groups, 2.01;

TABLE 1

NMR SPECTRA[a] OF THE ADDITION PRODUCTS, $Et_2Al{-}N{=}CR{-}NMe_2$, (III) AND (V)

R	No.	Chemical shift, τ (ppm)			
		CH_3CAl (t)	CCH_2Al (q)	NMe_2 (s)	Other protons[b]
C_6H_5	(IIIa)	8.70	10.05	7.38	
p-MeC_6H_4	(IIIb)	8.66	10.02	7.39	7.94(s) ($-CH_3$) (8.09)[b]
p-$NO_2C_6H_4$	(IIIc)[c]	8.63	9.81	7.40	
p-$MeOC_6H_4$	(IIId)	8.58	9.98	7.28	6.62(s)($-OCH_3$) (6.80)
p-$Me_2NC_6H_4$	(IIIe)	8.65	9.90	7.26	7.40(s)($-NMe_2$) (7.65)
CH_3	(Va)	8.64	9.80	7.43	8.08(s)($-CH_3$) (8.65)
$C_6H_5CH_2$	(Vb)	8.58	9.68	7.41	6.11(s)($-CH_2-$) (6.93)
	(Ia)	8.87	9.94	7.89	

[a] In 20% benzene solution containing internal standard TMS. [b] The chemical shifts (τ) of these protons in corresponding starting nitriles (II or IV) in parentheses. [c] Low concn. due to poor solubility in benzene.

TABLE 2

IR DATA[a] OF ADDITION PRODUCTS, $Et_2Al{-}N{=}CR{-}NMe_2$, (III) AND (V)

R		Assignment of key bands (cm^{-1})	
		$\nu(N{=}C{-}N)$	Other main absorption bands[b]
C_6H_5	(IIIa)	1573 (vs)	1065, 800, 665
p-MeC_6H_4	(IIIb)	1557 (vs)	1085, 830 (δ_{CH}), 759
p-$NO_2C_6H_4$	(IIIc)	1587 (s)[c]	1570 (s) (ν_{NO_2})[c], 1529[c], 1355, 870 (ν_{CN}), 845
p-$MeOC_6H_4$	(IIId)	1568 (vs)	1250 (ν_{Ar-OC}), 840
p-$Me_2NC_6H_4$	(IIIe)	1565 (vs)	1370 (ν_{Ar-NC}), 820
CH_3	(Va)	1578 (vs)	
$C_6H_5CH_2$	(Vb)	1571 (vs)	1140, 980

[a] In 2.5% benzene solution. [b] Absorptions at 2930, 2885, 2850, 1385–95, 1055 and 630 cm^{-1}, due to $AlEt_2$, always appeared in all above compounds. [c] We are contentious in these assignment [$\nu(NO_2)$ in (IIc) appeared at 1555 cm^{-1}].

mol. wt. cryoscop. in benzene, 454. $C_{13}H_{21}AlN_2$ calcd.: C, 67.21; H, 9.11; Al, 11.62%; active ethyl groups, 2.00; mol. wt. dimer, 464.)

Reaction of Et_2AlNMe_2 (Ia) with p-tolunitrile (IIb)

The reaction was carried out as with (IIa), but occurred more slowly. The ν(C≡N) absorption band had not disappeared after 6 h, but had almost done so after 12 h. The product was white crystalline, $Et_2Al\text{–}N{=}C(C_6H_4CH_3)\text{–}NMe_2$ (IIIb), m.p. 107–109°, yield 72%. (Found: C, 69.19; H, 8.02; mol. wt., 462. $C_{14}H_{23}AlN_2$ calcd.: C, 69.11; H, 8.28%; mol. wt. dimer, 488.) Downfield shifts of the signals due to proton of NCH_3 and p-CH_3 were observed in the NMR spectrum.

Reaction of Et_2AlNMe_2 (Ia) with p-nitrobenzonitrile (IIc)

The reaction took place more readily and the color changed in few hours from light yellow to black, even though the temperature was relatively low (40°). Black-brown crystalline (IIIc) was obtained quantitatively. It decomposed at 130–180°. Analytical data were consistent with a 1/1 addition product. (Found: C, 56.88; H, 7.31; Al, 9.08. $C_{13}H_{20}AlN_3O_2$ calcd.: C, 56.47; H, 7.18; Al, 9.71%.)

Reaction of Et_2AlNMe_2 (Ia) with p-methoxybenzonitrile (IId)

The reaction was carried out in benzene under the conditions described above. The band due to ν(C≡N) was strong even after 20 h. After continued heating at 80° for 72 h, and removal of unreacted (IId), white needles of (IIId), $Et_2Al\text{–}N{=}C(NMe_2)\text{–}C_6H_4OMe$, m.p. 130–132°, were obtained in 43% yield. (Found: C, 65.59; H, 8.89. $C_{14}H_{23}AlNO$ calcd.: C, 65.73; H, 8.84%.) Downfield shifts of the proton signals of NMe_2 and p-CH_3O were observed.

Reaction of Et_2AlNMe_2 (Ia) with p-(dimethylamino)benzonitrile (IIe)

In this reaction, after heating the mixture for 72 h, there was no indicating of any migration of the NMe_2 group. Further heating at 130° for 6 h gave greyish green crystalline product, $Et_2Al\text{–}N{=}C(C_6H_4NMe_2)\text{–}NMe_2$, m.p. 121–124° (recrystallized from n-hexane) in 20% yield. (Found: C, 65.53; H, 9.20; Al, 10.21. $C_{15}H_{26}N_3Al$ calcd.: C, 65.41; H, 9.52; Al, 9.80%.) Unreacted (Ia) had remained in the soluble part of n-hexane.

Reaction of Et_2AlSEt (Ib) with benzonitrile and its derivatives (IIa–e)

(IIa–e) (about 5–6 mmoles) in 3 ml of benzene was added to an equivalent amount of (Ib), under the conditions used for the reaction of (Ia) with IIa–e. The color of the mixture became gradually yellowish, and the ν(C=N) bond weakly appeared at 1550 cm^{-1}, but the starting (Ib), b.p. 100–102° (0.2 mm) was quantitatively recovered. The same results were obtained when solvent was omitted.

Reaction of Et_2AlNMe_2 (Ia) with acetonitrile (IVa)

(IVa) (9.1 mmoles) in benzene (3 ml) was added to (Ia) (9.0 mmoles). The reaction proceeded as rapidly as with (IIa), and white crystalline product $Et_2Al\text{–}N{=}C(CH_3)\text{–}NMe_2$, (Va), was precipitated after 20 h; it was recrystallized from n-hexane to give material of m.p. 111–115° in 44% yield. The NMe_2 and $=CCH_3$ proton signal in its NMR spectrum were shifted downfield. (Found: C, 56.26; H, 10.85; Al, 15.13;

active ethyl groups, 1.89; mol. wt. cryoscop. in benzene, 368. $C_8H_{19}AlN_2$ calcd.: C, 56.44; H, 11.25; Al, 15.86%; active ethyl groups, 2.00; mol. wt. dimer, 340.)

Reaction of Et_2AlNMe_2 (Ia) with benzyl cyanide (IVb)

The reaction was carried out as above, the ν(C≡N) bond disappearing after 20 h the resulting white needle-like crystalline product, recrystallized from n-hexane, $Et_2Al{-}N{=}C(NMe_2){-}CH_2C_6H_5$, (Vb), m.p. 106–108°, was obtained in yield 46%. (Found: C, 68.75; H, 8.51; mol. wt. cryoscop. in benzene, 465. $C_{14}H_{23}AlN_2$ calcd.: C, 69.11; H, 8.28%; mol. wt. dimer, 488.) A downfield shift of 0.82 ppm was observed for the signal being assignable to the methylene proton ($PhCH_2$).

Reaction of Et_2AlNMe_2 (Ia) with ethyl cyanoacetate (IVc)

In a preliminary experiment without solvent, these reacted explosively to give orange-colored powder. (Ia) (6.7 mmoles) in 5 ml of benzene was dropped slowly into (IVc) (6.7 mmoles) in 5 ml of benzene. The evolved gas was passed through concd. sulfuric acid and it was noted that the temperature and the color of the sulfuric acid did not change. The immediately precipitated product (VI) had an analysis consistent with the formula $C_9H_{17}AlN_2O_2$, which corresponds to loss of ethane. (Found: C, 52.16; H, 7.83; Al, 12.37. $C_9H_{17}AlN_2O$ calcd.: C, 50.93; H, 8.07; Al, 12.72%.) Its melting point was too high to measure in an usual manner.

Reaction of Et_2AlSEt (Ib) with acetonitrile (IVa)

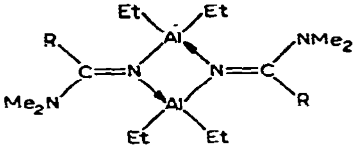
The reaction involving equimolar quantities gave the yellow powder (VII) (R = Me) in 53% yield. (Found: C, 40.80; H, 9.51; Al, 18.38. $C_8H_{18}AlNS$ calcd.: C, 41.30; H, 9.69; Al, 14.41%.) Physical measurements could not be made because of the low solubility in organic solvents.

RESULTS AND DISCUSSION

Wade *et al.*[7] reported the preparation of an interesting compound $Et_2Al{-}N{=}CH{-}NMe_2$, which was obtained either from the reaction between Et_2AlH and $Me_2N{-}C{\equiv}N$ or from the decomposition products of $Me_2NC{\equiv}N{\rightarrow}AlEt_3$ adduct. Products resulting from migration of the alkyl group, $R_2Al{-}N{=}CR{-}NMe_2$ (R = Me, Et), were not obtained.

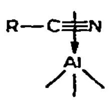
We found that in the reaction of Et_2AlX [X = NMe_2 (Ia), SEt (Ib)] with appropriate acceptor molecules such as isocyanates, the Al–X bond was cleaved and 1/1 addition products were formed. In addition, succesive insertion or addition–elimination reactions were observed to occur when phenyl isocyanate was used as the acceptor.

We have now found that the Al–N bond of (Ia) adds across the C≡N bond of (II) or (IV), as shown in eqns. (1) and (2), under the moderate reaction conditions. This 1/1 addition reaction takes place exclusively through Al–N bond cleavage of (Ia), and no product of Al–Et bond cleavage reaction is obtained. The Al–N bond fission was confirmed by the following evidence: (*a*). The IR spectra of the products (III) showed the strong absorption band at 1560–1580 cm^{-1} due to ν(N=C–N), instead of 2240 cm^{-1} due to ν(C≡N) found in the starting nitriles. (*b*). The NMe_2 proton signals in (Ia) in benzene, which occur at τ 7.89, shifted markedly downfield in products (III) and (V). (*c*). Definite downfield shifts were observed in the signals from p-CH_3(IIIb), p-CH_3O(IIId), p-$(CH_3)_2N$ (IIIe) and from the α-proton of (Va–b). (*d*). Analytical data were consistent with 1/1 addition product, except in the case of ethyl cyanoacetate. Four-membered coordination complexes such as those shown in (A) are well known; most of the cryoscopically measured molecular weights of the adducts (III) in benzene indicated a dimeric form.

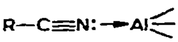


(A)

In spite of the differing ease of formation of the 1/1 addition products, all the reaction mixture gradually changed from colorless to light-yellow, red-brown or black at room temperature (30°), and this can be ascribed to interaction between the nitrile group and the Al atom. According to Wade *et al.*[2,11,12], when group IIIa organometallic compounds interact with nitriles, the absorption band at about 2240 cm^{-1} shift toward higher wave number. The $C{\equiv}N{\rightarrow}M$ ($M = B$, Al) bond in the coordination product $CH_3{-}C{\equiv}N{\rightarrow}MCl_3$ was found by Walton[13] to be linear in X-ray analysis. The information indicates that the coordination of the Al atom with the nitrile would not utilize the π-electrons of the C≡N triple bond, as in (B), but rather the lone-pair (n-electrons) on the nitrogen atom as in (C).



(B)



(C)

In Table 3, qualitative results in the relative reactivity of p-substituted benzonitriles are shown. The reactivity order is $NO_2 > H \simeq CH_3 > OMe > NMe_2$, *i.e.*, reactivity decreases with increase in electron release by the p-substituent. We thus suggest that the first step of these reactions is the formation of a σ-complex using the

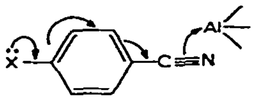
TABLE 3

RELATIVE REACTIVITIES IN THE REACTION OF Et_2AlNMe_2 WITH p-SUBSTITUTED BENZONITRILES, p-$X{-}C_6H_4{-}CN$[a]

Compound X	Color change[b]	Absorp.[d] at *ca.* 2240 cm^{-1} after				Yield[c] of (III) (%)
		6 h	12 h	20 h	72 h	
(IIc) NO_2	Very fast (black)	×				~100
(IIa) H	Fast (brown)	×				75
(IIb) Me	Fast (yellow)	○	×			72
(IId) MeO	Fast (yellow)	○	○	○	×	43
(IIe) Me_2N	Slow (brown)	○	○	○	○	0[e]

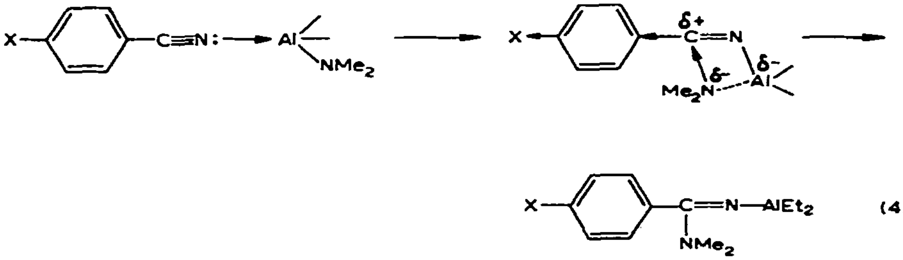
[a] Normal experimental condition; 80°, 20 h, except $X = NO_2$. [b] The mixture changed colour usually after the temperature had rosen to that of the room. [c] After 20 h. [d] (×) indicates disappearance of the C≡N band, and (○) its persistence. [e] (IIIe) was obtained after further heating to 130° without solvent.

lone-pair of the nitrogen atom, and that this is followed by nucleophilic attack of the NMe_2 group on the C atom of the C≡N bond. If the reaction occurred through the π-complex (B), as in D the reaction would be expected to be accelerated by electron-donating groups,



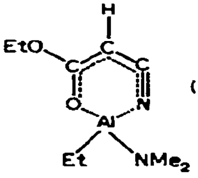
(D)

On the other hand, if the reaction occurs through the σ-complex (C), increase of π-electron density in the C≡N group by electron-donating *p*-substituents might hinder the nucleophilic migration of the NMe_2 group to the C atom of the cyano group, as in eqn. (4).



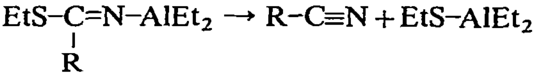
(4)

In acetonitrile derivatives, elimination of α-hydrogen atom accompanied by the evolution of ethane or dimethylamine would be expected to occur in competition with attack of the NMe_2 group on the C atom of the C≡N group. The latter reaction was predominant in the case of acetonitrile and benzyl cyanide, giving the product having the Al–N=CR–N structure. But the reaction between (Ia) and ethyl cyano-acetate gave ethane and a product of structure (E).



(E)

Contrary to its behaviour with isocyanates[4], Et_2AlSEt, (Ib) did react with nitriles, but the addition products could only be isolated in the case of acetonitrile. This suggests that after the formation of a σ-complex Al–S bond cleavage is more difficult than Al–N bond fission or alternatively that, addition products were formed, as indicated by the absorption band at about 1550 cm^{-1} in IR spectra of a few reaction mixtures, but with elimination as shown in eqn. (5) occurring during the distillation.



$$EtS\text{–}\underset{\displaystyle R}{\underset{|}{C}}\text{=}N\text{–}AlEt_2 \rightarrow R\text{–}C\equiv N + EtS\text{–}AlEt_2 \qquad (5)$$

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