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REACTIONS OF METHYLALUMINIUM COMPOUNDS WITH ACRYLONITRILE*

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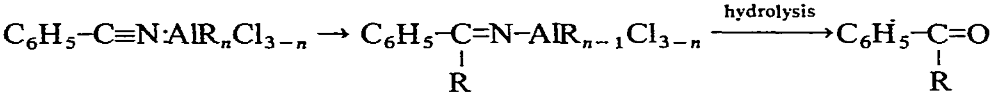
SUMMARY

The reactions of trimethylaluminium, dimethylaluminium chloride, and methylaluminium dichloride with acrylonitrile have been investigated. They have been found to afford equimolecular donor–acceptor complexes. The complexes react at elevated temperatures to yield methane and derivatives of dihydro and hexahydropyrimidine. The yields of the products of the methylaluminium compounds investigated have been studied in relation to the reaction temperature. Reaction mechanisms have been discussed in terms of the data obtained.

INTRODUCTION

In our previous investigations the reactions of organoaluminium compounds with benzonitrile were explored[1–6]. The donor–acceptor complexes thus obtained with organoaluminium compounds were found to react at elevated temperatures to yield corresponding ketimines, which on hydrolysis produced ketones:



$$C_6H_5{-}C{\equiv}N{:}AlR_nCl_{3-n} \rightarrow C_6H_5{-}\underset{R}{\underset{|}{C}}{=}N{-}AlR_{n-1}Cl_{3-n} \xrightarrow{\text{hydrolysis}} C_6H_5{-}\underset{R}{\underset{|}{C}}{=}O$$

$n = 1$–3

Reinheckel and Jahnke[7] and Lloyd and Wade[8] also have studied the reactions of organoaluminium compounds with benzonitrile and also with aliphatic nitriles[9]. The nitriles with the CN group on the tertiary carbon atom (*e.g.* tert-butyl cyanide) add to organoaluminium compounds in a way similar to benzonitrile. On the other hand, the nitriles with a hydrogen atom at the carbon atom α to the nitrile group (*e.g.* ethyl cyanide) yield addition products and eliminate the alkane from a given organoaluminium compound. Benzyl cyanide[10] reacts with organoaluminium compounds in a manner similar to that of aliphatic nitriles endowed with a mobile hydrogen atom.

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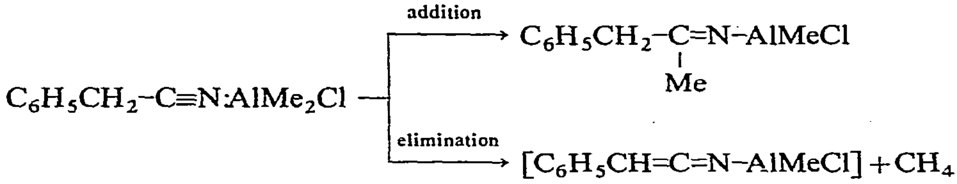
* Preliminary Note: see ref. 13.

With dimethylaluminium chloride, benzyl cyanide yields both the addition as well as the elimination product:



$$C_6H_5CH_2{-}C{\equiv}N{:}AlMe_2Cl \xrightarrow{\text{addition}} C_6H_5CH_2{-}\underset{\underset{Me}{|}}{C}{=}N{-}AlMeCl$$

$$C_6H_5CH_2{-}C{\equiv}N{:}AlMe_2Cl \xrightarrow{\text{elimination}} [C_6H_5CH{=}C{=}N{-}AlMeCl]+CH_4$$

The products of elimination have not been isolated; they may be subject to partial polymerization.

In this investigation the reactions of acrylonitrile with methylaluminium compounds were examined. Such reactions of acrylonitrile and other unsaturated nitriles have not yet been reported. Only Bogdanovič and Velič[11] described the reduction of acrylonitrile by diisobutylaluminium hydride at room temperature, which affords an allylideneimine derivative in high yield:

$$CH_2{=}CH{-}C{\equiv}N+HAl\text{-i-}Bu_2 \rightarrow CH_2{=}CH{-}CH{=}N{-}Al\text{-i-}Bu_2$$

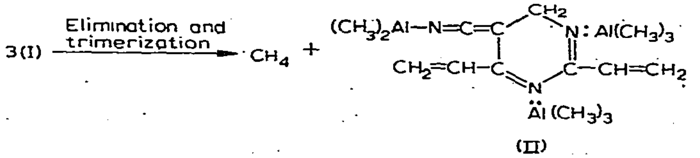
RESULTS

Reactions of acrylonitrile with trimethylaluminium, dimethylaluminium chloride, and methylaluminium dichloride were studied. They were carried out in the absence of solvents and also in aliphatic and aromatic hydrocarbons as solvents. The mole ratio of the reactants was 1/1, except for trimethylaluminium when it was 1/2. With these methylaluminium compounds, acrylonitrile was found to yield donor–acceptor complexes (1):

$$CH_2{=}CH{-}C{\equiv}N+Al(CH_3)_nCl_{3-n} \xrightarrow{\text{complexation}} \underset{\text{(I)}}{CH_2{=}CH{-}C{\equiv}N{:}Al(CH_3)_nCl_{3-n}} \quad (1)$$

$n=1\text{–}3$

As is evident from IR studies, the $\nu(C{\equiv}N)$ band at 2230 cm^{-1} in free acrylonitrile is shifted to 2275, 2280, and 2284 cm^{-1}, respectively, in the complexes with trimethylaluminium, dimethylaluminium chloride and methylaluminium dichloride. The complex (I) of each methylaluminium compound investigated was found to undergo reaction (2) involving elimination of methane and trimerization to a solid compound (II):



(2)

(II)

Irrespective of the methylaluminium compound used, the maximum yield of methane was 1 mole per 3 moles of complex (I) (Tables 1–3). As the reaction (2) progresses, the $\nu(C{\equiv}N)$ band in the complex (I) decreases in intensity. After all methane has evolved, the band disappears thus indicating completion of the reaction of the complex (I). A confirmatory evidence is found in the fact that, after calculated amount of methane was collected the hydrolyzed product contained no acrylonitrile. When methane was collected in amounts less than calculated, the reaction mixture contained some unreacted complex (I).

The course of both the elimination and trimerization reactions can be followed in terms of the volume of methane evolved. The rate of this reaction is related to the nature of methylaluminium compound, temperature, time, and other operating conditions.

The complex (I) of acrylonitrile with trimethylaluminium eliminates methane and trimerizes at a temperature of about 100°. In 1½ h the trimer (II) is obtained in about 100% yield (Table 1). The yield of the product of reaction (2) is presented in Fig. 1 in relation to time at various temperatures. The elimination and trimerization reactions can follow an uncontrolled course (Table 1) if run without any solvent. The presence of a solvent (xylene) in the reaction mixture protracts the reaction time and affects its course (Fig. 2). With trimethylaluminium used in excess (acrylonitrile/

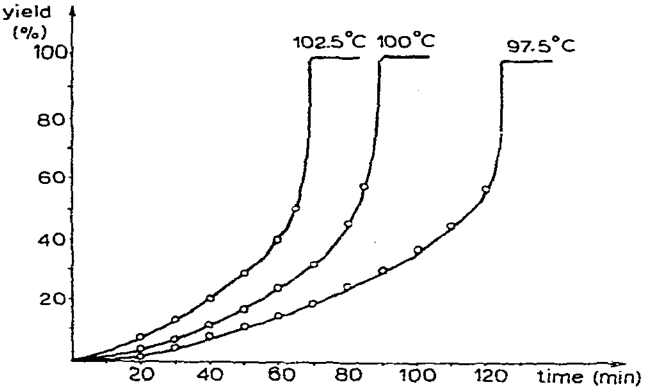


Fig. 1. The extent of elimination and trimerization (2) in the reaction of acrylonitrile with trimethylaluminium as a function of time (reactant mole ratio 1/1, no solvent).

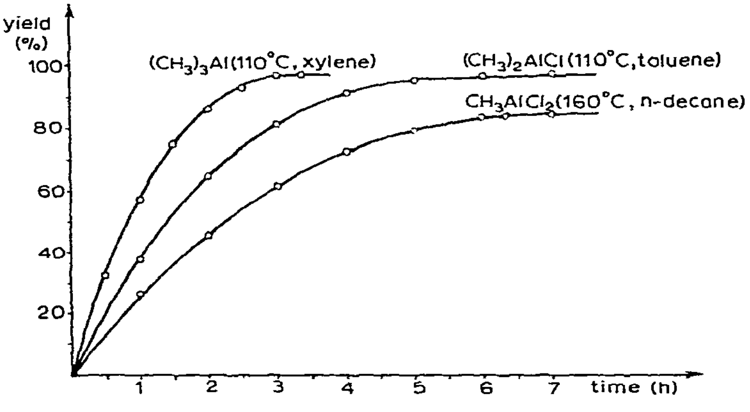


Fig. 2. The extent of elimination and trimerization (2) in the reactions of acrylonitrile with trimethylaluminium, dimethylaluminium chloride, and methylaluminium dichloride as a function of time (reactant mole ratio 1/1, solvent).

(continued p. 348)

TABLE 1

REACTION OF TRIMETHYLALUMINIUM WITH ACRYLONITRILE

Me_3Al		Me_3Al/ CH_2CHCN, by moles	Solvent (ml)	Reaction		CH_4 evolved on		CH_4 from Me_3Al (ml)[a]	Yield of reaction	
(g)	(mmoles)			Temp. (°C)	Time (min)	Reaction (ml)	Hydrolysis (ml)		Elimination and trimerization (2)[b] (%)	Addition (3)[c] (%)
1.08	15.0	1/1		97.5	125	109	667	1008	97.3	97.3
0.91	12.7	1/1		100	90	94	560	853	98.9	98.9
0.87	12.1	1/1		100	80	88	538	813	97.3	97.3
0.86	12.0	1/1		100	80	87	533	806	97.1	97.1
1.08	15.0	1/1		100	85	108	665	1008	96.4	96.4
0.79	11.0	1/1		102.5	70	81	487	739	98.5	98.5
3.99	55.4	1/1		100	50	[d]		3723		
1.16	16.1	1/1	Toluene (3)	100	140	118	790	1082	98.2	72.3
10.09	140.1	1/1	Xylene (100)	110	200	1013	7332	9414	96.8	51.1
10.80	150.0	1/1	Xylene (100)	120	120	1094	7635	10080	97.7	60.3
0.59	8.2	2/1		95	40	30		551	96.1	
1.77	24.6	2/1		20	18 h	12		1653	13.1	
1.76	24.6	2/1		20	146 h	77		1640	85.5	

[a] Theoretical amount of methane to be evolved on hydrolysis of the trimethylaluminium added to the reaction mixture. [b] Based on the acrylonitrile–trimethylaluminium complex according to eqn. (2). [c] Based on the acrylonitrile–trimethylaluminium complex according to eqn. (3). [d] Vigorous reaction with methane evolving in considerable amounts.

TABLE 2. REACTION OF DIMETHYLALUMINIUM CHLORIDE WITH ACRYLONITRILE

Me_2AlCl		Me_2AlCl/CH_2CHCN, by moles	Solvent (ml)	Reaction		CH_4 evolved on		CH_4 from Me_2AlCl (ml)[a]	Yield of reaction	
(g)	(mmoles)			Temp. (°C)	Time (h)	Reaction (ml)	Hydrolysis (ml)		Elimination and trimerization (2)[b] (%)	Addition (3)[c] (%)
1.69	18.3	1/1		−10	3	4	810	820	2.8	2.2
1.69	18.3	1/1		20	3	7	807	820	5.1	2.2
1.69	18.3	1/1		50	3	16	796	820	11.8	2.9
1.69	18.3	1/1		80	3	29	785	820	21.2	2.2
1.69	18.3	1/1		80	9	77	737	820	56.5	2.2
1.69	18.3	1/1		110	3	112	679	820	82.5	10.7
1.69	18.3	1/1		110	7	134		820	98.5	
1.69	18.3	1/1		130	2	135	635	820	99.0	18.2
1.69	18.3	1/1		135	1	[d]		820		
17.39	188.0	1/1	Toluene (17)	110	3	1136		8422	81.0	
17.39	188.0	1/1	Toluene (17)	110	7	1356	6050	8422	96.7	36.2
18.75	202.7	1/1	Xylene (70)	130	6	1472		9081	97.3	
21.89	236.6	1.3/1		80	16	1303	9269	10600	96.1	1.0

[a] Theoretical amount of methane to be evolved on hydrolysis of the dimethylaluminium chloride added to the reaction mixture. [b] Based on the acrylonitrile–dimethylaluminium chloride complex according to eqn. (2). [c] Based on the acrylonitrile–dimethylaluminium chloride complex according to eqn. (3).[d] Vigorous reaction with methane evolving in considerable amounts.

TABLE 3. REACTION OF METHYLALUMINIUM DICHLORIDE WITH ACRYLONITRILE

$MeAlCl_2$		$MeAlCl_2/CH_2CHCN$, by moles	Solvent (ml)	Reaction		CH_4 evolved on		CH_4 from $MeAlCl_2$ (ml)[a]	Yield of reaction	
(g)	(mmoles)			Temp. (°C)	Time (h)	Reaction (ml)	Hydrolysis (ml)		Elimination and trimerization (2)[b] (%)	Addition (3)[c] (%)
1.35	12.0	1/1		130	6	25	228	268	28.1	8.4
1.35	12.0	1/1		150	6	70	150	268	78.4	27.0
1.35	12.0	1/1		150	6	67	149	268	75.3	29.2
1.35	12.0	1/1		170	6	70	134	268	78.4	36.0
4.68	41.5	1/1	n-Decane (65)	160	7	260		929	83.9	

[a] Theoretical amount of methane to be evolved on hydrolysis of the methylaluminium dichloride added to the reaction mixture. [b] Based on the acrylonitrile methylaluminium dichloride complex according to eqn. (2). [c] Based on the acrylonitrile–methylaluminium dichloride complex according to eqn. (3).

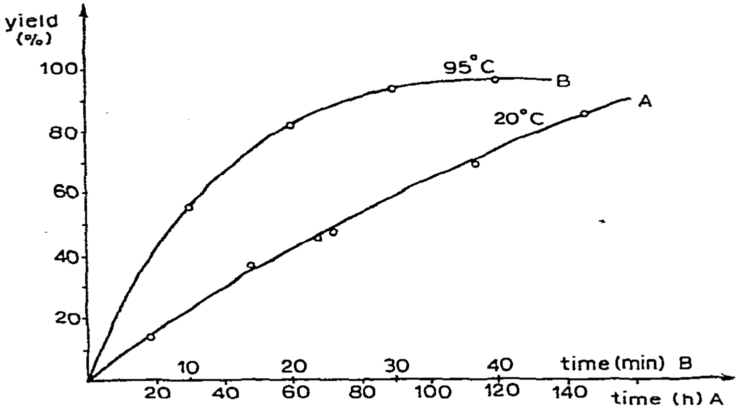


Fig. 3. The extent of elimination and trimerization (2) in the reaction of acrylonitrile with trimethylaluminium as a function of time (reactant mole ratio 1/2, no solvent).

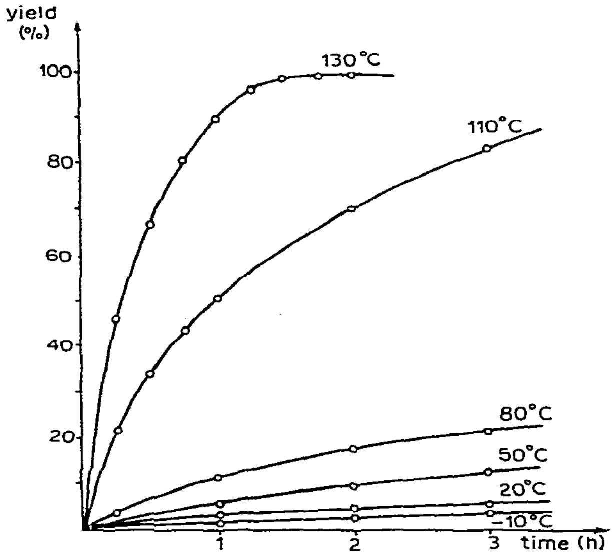


Fig. 4. The extent of elimination and trimerization (2) in the reaction of acrylonitrile with dimethylaluminium chloride as a function of time (reactant mole ratio 1/1, no solvent).

trimethylaluminium 1/2 by moles), the temperature is reduced and the reaction accelerated (Table 1; Fig. 3).

The complex (I) of acrylonitrile with dimethylaluminium chloride eliminates methane and trimerizes less readily than does the complex with trimethylaluminium. For example, it is only after 7 h at 110° that the trimer (II) is obtained in about 100% yield (Table 2). The yield of the product of reaction (2) is presented in Fig. 4 in relation to time at various temperatures. The yield of the trimer (II) rises as the temperature is increased, similarly as is the case with the trimethylaluminium complex. With no solvent used, the elimination and trimerization fails to proceed so vigorously as it does with trimethylaluminium as reactant. Only at 135° does it follow an uncontrolled course (Table 2). The presence of a solvent (toluene) affects only insignificantly the type and time of this reaction (Fig. 2).

The complex (I) of acrylonitrile and methylaluminium dichloride eliminates methane and trimerizes still less readily than the corresponding trimethylaluminium and the dimethylaluminium chloride complexes. The extent of the elimination and trimerization reaction (2) fails to attain a value of 100%. In 6 h at 130°, it is as low as 28.1% and at 150° (6 h) it is about 78% (Table 3). A further increase in temperature has a slight effect on the reaction yield. At elevated temperatures (170°) the reaction proceeds faster only during its initial stage (Fig. 5). Similarly as for the dimethylaluminium chloride complex (I), the presence of a solvent (n-decane) slightly affects the reaction rate (Fig. 2). In addition to the elimination and trimerization (2) reactions the acrylonitrile–methylaluminium dichloride complex (I) undergoes a side reaction at elevated temperatures. In the IR spectra of the products obtained at a temperature of 150° and higher, the band characteristic of the complexed nitrile group disappears. This fact indicates that the complex (I) has reacted completely, though the yield of the major reaction (2) is lower than theoretical (amounts to about 80%). This side reaction presumably involves oligomerization of the complex (I) through the nitrile groups and no evolution of methane.

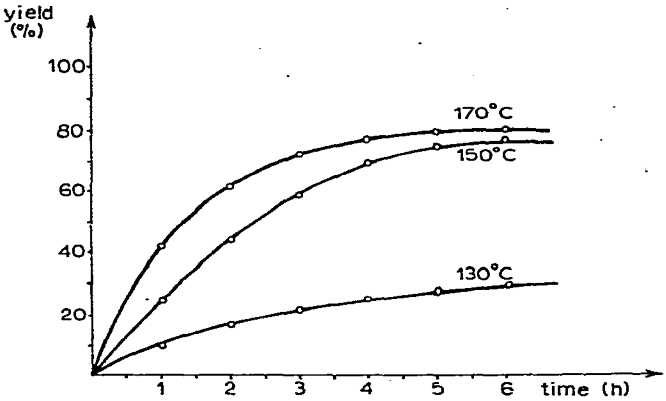
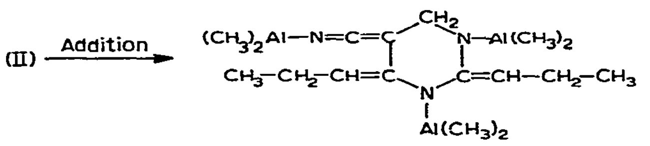


Fig. 5. The extent of elimination and trimerization (2) in the reaction of acrylonitrile with methylaluminium dichloride as a function of time (reactant mole ratio 1/1, no solvent).

In contrast to the reported complexes of nitriles with alkylaluminium compounds[1-10] and of the complex of acrylonitrile with diisobutylaluminium hydride[11], the complexes (I) of acrylonitrile with all the methylaluminium compounds investigated undergo no addition reactions. No methyl vinyl ketone was found after the hydrolysis of the reaction mixture.

Addition does not proceed until the product (II) has formed. This is a donor–acceptor complex of the trimer with two molecules of the organoaluminium compound. The addition (3) affords compound (III):



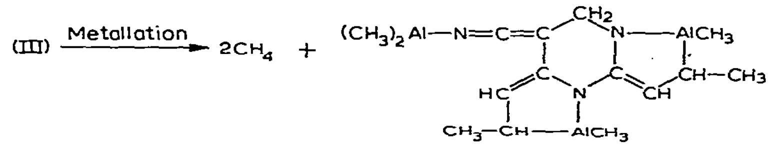
(3)

(III)

The extent of this addition reaction is calculated as the difference between the theoretical amount of methane to be evolved during the hydrolysis of the organoaluminium compound allowed to react and the combined amount of methane evolved during the reaction (2) and on the hydrolysis of the products of the reaction (3).

Addition (3) proceeds most easily with the complex (II) of trimethylaluminium and at 100° it attains a yield of about 100% (Table 1). Much less readily occurs this reaction with the complex (II) of dimethylaluminium chloride and in 2 and 7 h at 130° and 110° (in toluene) the yields are 18.2 and 36.2%, respectively (Table 2). At 80° and less, the addition practically fails to proceed. The slowest one to react is the complex (II) of methylaluminium dichloride. With this complex after 6 h at 130° and 170°, addition (3) attains yields of only 8.4 and 36.0%, respectively (Table 3).

In an oxygen- and water-free atmosphere, the product (III) of the reaction between acrylonitrile and trimethylaluminium is stable up to 180°. On being heated for 15 min at that temperature, it does not release methane. At temperatures higher than 180°, it metallates itself (4) and yields methane and a compound (IV):



(4)

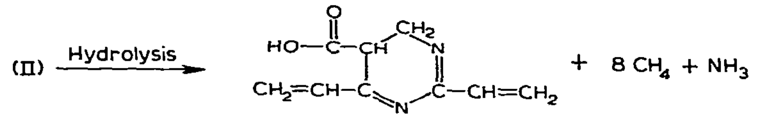
(IV)

The metallation (4) can be followed in terms of the amount of evolved methane. At 200°, it proceeds slowly and with difficulty (at that temperature it attains a yield of 22% in 30 min). At higher temperatures the rate of this reaction increases and, with the temperature raised progressively from 200° to 280°, the product (IV) is obtained in about 100% yield in 3 h. Prolonged heating of the metallate (IV) at temperatures up to 300° results in continued evolution of methane due to thermolysis of the methylaluminium compound. A partial thermolysis can occur simultaneously with the metallation (4).

All products (II) and (III) of the reactions of acrylonitrile with the methylaluminium compounds investigated are yellow solids. They are likely to form intermolecular compounds via bridges incorporating aluminium and nitrogen atoms. The poor solubility of these products in neutral solvents (hydrocarbons) prevented further examination.

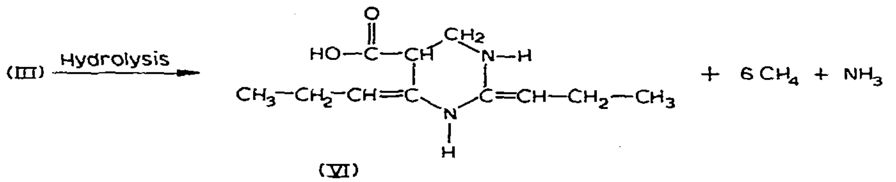
IR studies on the products of the reaction of acrylonitrile with dimethylaluminium chloride [a mixture of compounds (II) and (III)] revealed, among other things, the presence of bands at 1650 and 2200 cm^{-1}. The former is attributable to the ring-borne $\rangle$C=N- groups and the latter to the -N=C=C$\langle$ substituents.

Compounds (II) and (III) are easily hydrolyzed, (5) and (6), by water and alcohol.



(5)

(V)



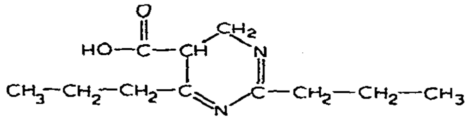
(VI)

(6)

The compound (VI) isolated from the mixture of products of the reaction between acrylonitrile and dimethylaluminium chloride analyzed as: Found: C, 64.34; H, 7.20; N, 13.35; O (by diff.), 15.11. $C_{11}H_{18}N_2O_2$ calcd.: C, 62.83; H, 8.63; N, 13.32; O, 15.22%.

On hydrolysis, the metallate (IV) (a greyish-brown solid) yielded compound (VI).

Compound (VI) can exist at equilibrium with its tautomer (VIa).

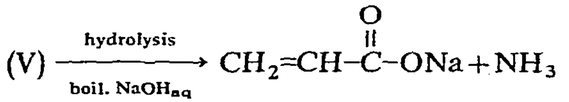


(VIa)

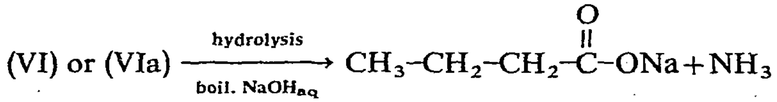
The hydrolysis products (V) and (VI) are yellow solids. They are very likely to occur in the form of internal salts owing to interaction of the carboxyl proton with the ring-borne nitrogen atoms. A presumptive evidence is indicated by the presence of characteristic bands at 2200 and 2240 cm^{-1} in the IR spectra of these products.

In addition, compounds (V) and (VI) occur as monomers or polymers according as they are prepared by hydrolysis with or without a polymerization inhibitor. Monomeric (V) and (VI) are soluble in water, methanol, and ethanol. With hydrogen chloride, they produce hydrochlorides and, owing to the presence of the carboxyl group, they react with alkalies to yield sodium or potassium salts. In the IR spectra of these salts, the 2200 and 2240 cm^{-1} bands are no longer present. Sodium salts are also produced in the reaction with sodium bicarbonate, accompanied by evolution of carbon dioxide from the bicarbonate. On heating, the monomers (V) and (VI) are readily polymerized. These polymers are insoluble in water and alcohol; but are soluble in dimethylformamide, dimethylsulphoxide, mineral acids, organic acids and in their aqueous and alcoholic solutions (as corresponding salts).

In boiling aqueous sodium or potassium hydroxide, compounds (V) and (VI) hydrolyse readily to release ammonia and corresponding acrylate (7) or butyrate (8) which, upon acidification, yield the free acids.



$$\text{(V)} \xrightarrow[\text{boil. NaOH}_{aq}]{\text{hydrolysis}} CH_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONa + NH_3 \qquad (7)$$



$$\text{(VI) or (VIa)} \xrightarrow[\text{boil. NaOH}_{aq}]{\text{hydrolysis}} CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONa + NH_3 \qquad (8)$$

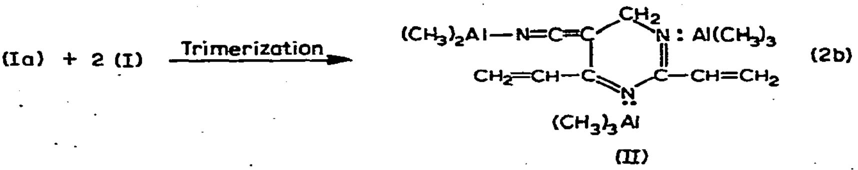
The hydrolysis of (VI) gave no methyl vinyl ketone. It proves that the methyl group in the trimer (II) rearranges exclusively by scheme (3) and does not migrate to the ring carbon atom of $\rangle C{=}N{-}$ group.

DISCUSSION

The reactions of acrylonitrile with methylaluminium compounds follow a different course from that reported for analogous reactions of other nitriles. Complexes (I) of acrylonitrile with the methylaluminium compounds investigated do not undergo addition reaction and do not give ketimine derivatives (methyl vinyl ketimines), unlike complexes of benzonitrile or aliphatic nitriles with organoaluminium compounds. They enter exclusively into the elimination and trimerization, reactions (2) which affords methane and the trimer (II).

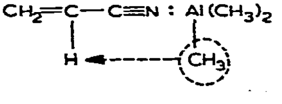
The present results are suggestive of a two-step mechanism for the reaction (2). The first step, (2a), involves elimination of methane from the complex (I) and formation of an unisolated intermediate compound (Ia). In the second step, (2b), the highly unstable intermediate (Ia) immediately reacts with two molecules of the complex (I) to yield the trimer (II):

$$\underset{\text{(I)}}{CH_2{=}CH{-}C{\equiv}N : Al(CH_3)_3} \xrightarrow{\text{Elimination}} CH_4 + \underset{\text{(Ia)}}{[CH_2{=}C{=}C{=}N{-}Al(CH_3)_2]} \quad (2a)$$



(II)

The elimination (2a) of methane presumably involves an attack of the methyl group and its solitary electron pair on the hydrogen atom in the complex (I):



(I)

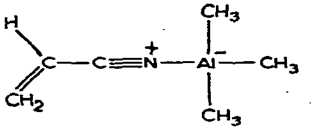
The experimental data showed that at elevated temperatures the reactivity of the methylaluminium compounds towards acrylonitrile follows the order:

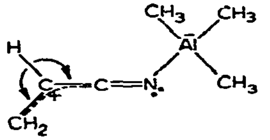
$$MeAlCl_2 < Me_2AlCl < Me_3Al$$

In keeping with the above series, the acid strength of the organoaluminium compound decreases and its ability to split off the methyl group increases. Should the elimination (2a) of methane occur by the attack of a proton on the methyl group, the reactivity of the methylaluminium compounds would increase in the reverse direction. Another confirmation of the suggested elimination (2a) scheme is the fact that the reaction of acrylonitrile with trimethylaluminium proceeds more readily with the latter reactant used in excess. This is in accordance with our earlier data concerning the reaction of benzonitrile with trimethylaluminium[3].

The elimination (2a) of methane proceeds smoothly and with high yields at elevated temperatures. At room temperature, it occurs much less readily.

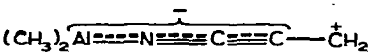
The structures of the complexes of nitriles with organoaluminium compounds have already been discussed[4,5]. On this basis, the structures of the acrylonitrile–trimethylaluminium complex at room and elevated temperatures can be represented by the following formulae, (IA) and (IB):


(IA)


(IB)

As evident from these formulae, the geometrical structure and charge distribution are more favourable to elimination of methane at elevated (IB) than at room temperature (IA).

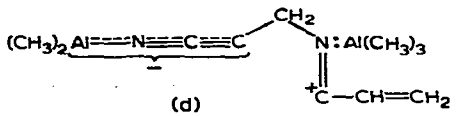
The resulting first-step intermediate (Ia) is highly polarized towards the aluminium atom:



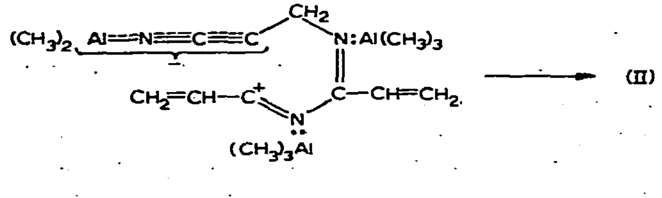
$$(CH_3)_2Al\cdots N\cdots C\cdots C-\overset{+}{C}H_2$$

(Ia)

The cumulated double bond system is conductive to polarization. As the result of polarization, the terminal carbon atom has acquired a strong positive charge and reacts with the acrylonitrile complex (I) immediately to yield a trimer (II). Trimerization presumably begins by an attack of the positively charged carbon atom on the complex (IA) molecule at the site of the highest charge density, *i.e.* on the triple bond C≡N. As a result, an intermediate dimer (d) is formed which, by its positive pole, attacks a second molecule of the complex (IA):

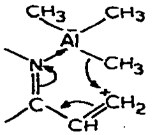

(d)

The resulting trimer (t) stabilizes itself by closing the six-membered ring of a dihydropyrimidine derivative to yield ultimately the cyclic trimer (II):


(t)

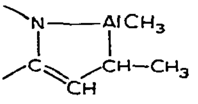
Trimerization (2b) proceeds much faster than does elimination (2a). Therefore, the maximum amount of methane evolved is 1 mole per 3 moles of complex (I). The trimerization of complex (I) fails to proceed, unless preceded by elimination of methane.

The cyclic trimer (II) is a donor–acceptor complex in which two nitrogen atoms link up two molecules of the organoaluminium compound. In this form the trimer undergoes addition. This involves migration of the methyl group and its electron pair to the positively charged carbon atom of the vinyl group. The centre of the addition may be formulated as follows:

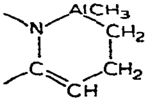


All the formerly established rules[12] for addition of organoaluminium compounds are applicable to the above case.

The metallation of the addition product (III) at a temperature higher than 180° was not studied in detail. Of the two possible modes of eliminating methane, either in the seven- or in the eight-centred system, the former appears to be the more plausible, leading to the product (IVA), rather than (IVB).



(IVA)



(IVB)

EXPERIMENTAL

1. *Materials*

The methylaluminium compounds were prepared by conventional procedures. Before use, they were thoroughly purified, *viz.*, trimethylaluminium and dimethylaluminium chloride by distillation and methylaluminium dichloride by crystallization from n-heptane.

Pure acrylonitrile (VEB Berlin-Chemie, Berlin–Adlershof) was distilled from phosphorus pentoxide in a nitrogen atmosphere and stored over molecular sieves (type 4A).

Commercial organic solvents were purified conventionally and stored over molecular sieves (type 4A) in a nitrogen atmosphere.

2. *Method*

Reactions were carried out in a three-neck 30-ml (or 200-ml) flask equipped with a stirrer and a cold trap connected through a small paraffin-oil wash-bottle to a gas burette. Before each reaction the set-up was repeatedly flushed out with dried deoxygenated nitrogen. Reactants were introduced into the flask by means of hypodermic syringes (except for methylaluminium dichloride which was added in ampoules) in the sequence: methylaluminium compound, solvent, and acrylonitrile. On dropwise addition of acrylonitrile (complexation), the reaction mixture was vigorously stirred and cooled.

The flask was placed in a thermostatted oil-bath at a specified temperature and it was connected to the gas burette. Volume of the evolving gas was measured at intervals in the burette with due allowance for temperature changes in the flask and reduced to standard conditions. After the reaction had been completed, the mixture was cooled and hydrolyzed at ambient temperature. In a few experiments, the final stages of hydrolysis were carried out at elevated temperatures. If the reaction was run with no solvent, petroleum ether was added in some experiments to the flask before hydrolysis. Aqueous 10% sodium hydroxide, water, methanol, or methanol containing 0.5% of hydroquinone were used for hydrolysis.

The volume of the gas evolved during hydrolysis was measured similarly as during the reaction. The volumes of the gas (methane) liberated during the reaction and during hydrolysis were used for calculating the yields of elimination and trimerization (2), addition (3), and metallation (4) using the following formulae:

$$\text{reaction (2) (\%)} = (3n/m) \cdot (x/z) \cdot 100,$$
$$\text{reaction (3) (\%)} = (3n/2m) \cdot [1-(x+y)/z] \cdot 100,$$
$$\text{reaction (4) (\%)} = (3n/2m) \cdot (x/z) \cdot 100 = 450 \cdot (x/z),$$

where n = the number of methyl groups in the molecule of methylaluminium compound ($n=1$, 2, and 3 for methylaluminium dichloride, dimethylaluminium chloride, and trimethylaluminium, respectively),
m = the acrylonitrile/methylaluminium compound mole ratio,
x = the volume of methane evolved during the reaction, ml (S.T.P.),
y = the volume of methane evolved during the hydrolysis, ml (S.T.P.),
z = the volume of methane evolved during the hydrolysis of the methylaluminium compound added to the reaction mixture, ml (S.T.P.).

3. *Analysis and identification of products*

Gaseous products (methane) were identified on a Chrom II gas chromatograph.

Analyses for acrylonitrile and methyl vinyl ketone in the hydrolyzed reaction mixtures and for acrylic acid, butyric acid, and methyl vinyl ketone in the products of alkaline hydrolysis at the boiling temperature (upon acidification) were carried out on a Carlo Erba gas chromatograph.

IR studies and analyses of the reaction mixture for complexes of acrylonitrile with methylaluminium compounds were carried out in hydrocarbon solutions. Spectra of the reaction products of acrylonitrile with the methylaluminium compounds, before and after hydrolysis, were run by the potassium bromide pellet technique or as Nujol mulls. All the spectra were recorded on a Zeiss UR-10 spectrophotometer.

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