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REACTIONS OF METHYLALUMINIUM COMPOUNDS WITH ACETONITRILE

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Summary

Reactions of methylaluminium compounds, particularly methylaluminium dichloride, with acetonitrile have been studied. The reactions were found to afford methane and aluminium derivatives of two isomeric acetonitrile trimers. These derivatives on hydrolysis give 2-amino-3-cyano-4-imino-2-pentene and 1-cyano-2-amino-4-imino-2-pentene or their oxygenated analogues, depending on prevailing hydrolysis conditions. An excess of acetonitrile over methylaluminium dichloride was found to favour, and a deficit of acetonitrile to inhibit, the elimination of methane. In the latter case, besides methane and acetonitrile trimerization products, a ketimine derivative is formed, which on hydrolysis yields acetone. When dimethylaluminium chloride and trimethylaluminium are used in 1/1 mole ratios with acetonitrile, corresponding ketimine derivatives are obtained in small yields in addition to methane elimination products. A mechanism for the methane elimination which yields acetonitrile trimerization products is suggested.

Introduction

Nitriles having an $H(C_\alpha)$ atom can react with aluminium alkyls to eliminate the corresponding alkane [1]. Wade et al. [2] have treated trimethylaluminium and dimethylaluminium chloride with acetonitrile. They found that, apart from addition which affords a corresponding ketimine derivative in slight yield, elimination of methane occurs, which also yields unidentified polymeric by-products. In the presence of inorganic metal chlorides, acetonitrile trimerizes to produce 4-amino-2,6-dimethylpyrimidine in slight yield and also polymerizes (it is suggested that the pyrimidine rings are involved in the polymer structure [3]).

The present work has been undertaken in an attempt to determine the products and to elucidate the nature of methane elimination in the reactions of methylaluminium compounds, in particular methylaluminium chlorides with acetonitrile; it was hoped that by using the chlorides, the side reaction of addition leading to ketimine derivatives would be suppressed.

TABLE 1

YIELDS OF METHANE AND ACETONE IN THE REACTIONS OF METHYLALUMINIUM COMPOUNDS WITH ACETONITRILE

Me_nAlCl_{3-n}	Nitrile/Me_nAlCl_{3-n} mole ratio	Temp. (°C)	Time (h)	Yield (%) [a]	
				CH_4	$(CH_3)_2C{=}O$
Me_3Al	1/1	130	6		16
Me_3Al	1/1	120-150	5	60 [b]	15-20 [b]
Me_2AlCl	1/1	160-165	5		7 [b]
Me_2AlCl	1/1	120	12	65	7
$MeAlCl_2$	1/1	170	12	80	
$MeAlCl_2$	1/1	170	6	65	
$MeAlCl_2$	1/2	170	16	5	4
$MeAlCl_2$	2/1	120	3	85	
$MeAlCl_2$	3/1	120	4	83	
$MeAlCl_2$	4/1	120	6	80	
$MeAlCl_2$	5/1	120	6	81	

[a] Based on the CH_3CN/Me_nAlCl_{3-n} complex I (per single methyl group). [b] Cf. ref. 2.

Results and discussion

Me_3Al, Me_2AlCl and $MeAlCl_2$ were found to form donor-acceptor complexes with acetonitrile (as with other nitriles) $CH_3{-}C{\equiv}N{\rightarrow}Al(CH_3)_nAlCl_{3-n}$ (I) ($n = 1, 2, 3$) stable at room temperature. IR spectra showed that, in the complexes I with $n = 1, 2$, and 3, the 2255 cm^{-1} nitrile band characteristic of free acetonitrile is shifted to 2307, 2303 and 2297 cm^{-1}, respectively.

At elevated temperatures, the complexes I undergo methane elimination. With Me_3Al and Me_2AlCl, the elimination is accompanied by a side reaction of addition which leads to acetone after hydrolysis. With the $MeAlCl_2/CH_3CN$ complex, no acetone is produced, unless $MeAlCl_2$ is used in excess of acetonitrile, when it is obtained in slight yields (Table 1). As regards addition, the results are similar to those obtained in the reactions of methylaluminium compounds with other nitriles [4, 5].

Besides methane, the elimination affords acetonitrile trimer derivatives. Hydrolyzates of the product mixtures of the $CH_3CN/MeAlCl_2$ reactions carried out at 1/1 and > 1 reactant mole ratios were found to contain 2-amino-3-cyano- and 1-cyano-2-amino-4-imino-2-pentenes or their oxygenated derivatives (depending on hydrolysis conditions) in about 2/1 ratio. No acetonitrile dimer derivatives could be separated from the products*.

These results indicate that elimination of methane is associated with trimerization of acetonitrile, and the yield of methane may be considered as a measure of the yield of the resulting trimers. Reactant mole ratio is the major factor governing the reaction course, as is evident from the reaction between $MeAlCl_2$ and CH_3CN (Table 1). With I ($n = 1$) (reactant mole ratio 1/1), elimination of methane is comparatively reluctant to occur, nevertheless its yield is high and even attains 80%, when an excess of acetonitrile is used. Conversely, a deficit of CH_3CN with respect to $MeAlCl_2$ has an adverse effect and the yield of methane drops to a mere few percent. This regularity observed with the elimination reactions is the opposite of that found with the addition reactions, suggesting the different nature of the two processes.

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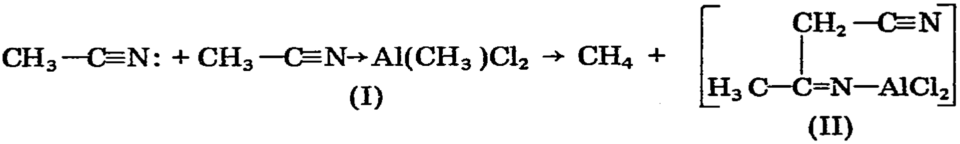
* Dimers were obtained in the methylaluminium dichloride/phenylacetonitrile reaction [6].

The results obtained suggest that, rather than proceeding intramolecularly within the complex I (eqn. 1), the elimination reaction follows a more complicated

$$\underset{\mathrm{(I)}}{\mathrm{CH_3{-}C{\equiv}N{\rightarrow}Al(CH_3)Cl_2}} \rightarrow [\mathrm{CH_2{=}C{=}N{-}AlCl_2}] + \mathrm{CH_4} \tag{1}$$

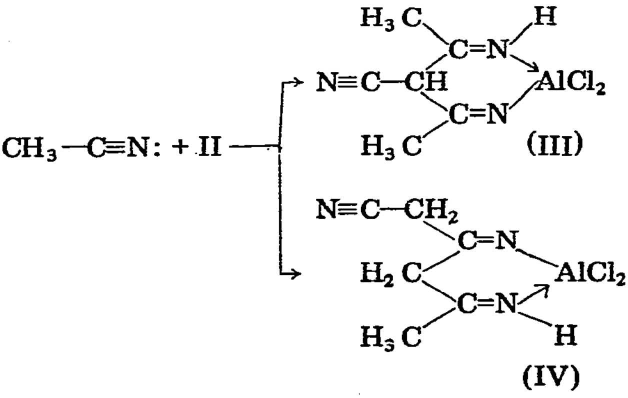
course involving more than one nitrile molecule per methylaluminium dichloride molecule, at least in those cases when the reactions are carried out with excess acetonitrile. The nitrile excess seems to be needed to solvate the equimolecular complex I. In the solvated complex I, interaction of the mobile hydrogen atom with an uncomplexed nitrile group may easily result in elimination of methane (eqn. 2).



$$\mathrm{CH_3{-}C{\equiv}N{:}} + \underset{\mathrm{(I)}}{\mathrm{CH_3{-}C{\equiv}N{\rightarrow}Al(CH_3)Cl_2}} \rightarrow \mathrm{CH_4} + \underset{\mathrm{(II)}}{\left[\begin{array}{l} \qquad \mathrm{CH_2{-}C{\equiv}N} \\ \qquad | \\ \mathrm{H_3C{-}C{=}N{-}AlCl_2} \end{array}\right]} \tag{2}$$

Evolution of methane in reaction 2 may well render one of its stages irreversible and thus enable CH_3CN to dimerize more easily in the presence of $MeAlCl_2$ than inorganic metal chlorides*.

II, possessing mobile hydrogen atoms in both the methylene and the methyl groups, reacts readily with a second CH_3CN molecule. The reaction proceeds in two directions depending on which hydrogen has attacked the nitrile group (eqn. 3a, b).



(3a)

(3b)

Such additions of the imidoalane C_α—H bond to the nitrile group have recently been described [7-9]. Obviously, the methylene hydrogen atoms in II are more mobile than the methyl's and reaction 3a should proceed with higher yields than 3b, which is borne out by the experimental data. Mobility of the hydrogen atoms in I, though considerably enhanced as compared with that in the uncomplexed nitrile, is much lower than in II. This fact causes the trimerization (eqns. 3a, b) to proceed at much faster rates than does the dimerization (elimination) (eqn. 2). This consideration makes it conceivable that the products of the $CH_3CN/MeAlCl_2$ reaction are always acetonitrile trimer derivatives, except when $MeAlCl_2$ is used in excess. As regards stoichiometry,

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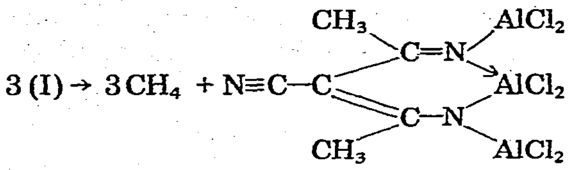
* At 120°, acetonitrile practically fails to react in the presence of $AlCl_3$.

reactions 2 and 3 involve the nitrile/methylaluminium compound mole ratio 3/1, with 1 mole of methane evolving per 1 mole of trimer formed. As the reactant mole ratio is decreased to 1/1, the reaction proceeds less readily because of the impeded attack of the nitrile group (complexed with methylaluminium dichloride) on the mobile hydrogen atom in a second complex molecule. In this case the quantity of methane evolved is three times the number of trimer moles as the result of formation of more $AlCl_2$-substituted trimers (eqn. 4). The trisubstituted aluminium derivative of the trimer IV should form in an analogous manner.



(4)

Irrespective of the starting reactant mole ratio, hydrolysis of the isomers III and IV leads to formation of 2-amino-3-cyano- and 1-cyano-2-amino-4-imino-2-pentenes, respectively, or to their oxygenated derivatives, depending on the hydrolysis conditions.

Experimental

Materials

The methylaluminium compounds were prepared by conventional methods and purified by distillation (Me_3Al and Me_2AlCl) and crystallization from heptane ($MeAlCl_2$). Commercial reagent-grade CH_3CN was purified by distillation.

Procedure

Each reaction was carried out under a nitrogen atmosphere in a 100-200 ml three-necked flask equipped with a stirrer and a cold trap, connected through a liquid seal to a gas burette. A methylaluminium compound, 10 to 20 g, was placed in the flask and CH_3CN added with simultaneous stirring and cooling. Then the reaction mixture was heated in a thermostatted bath. The methane evolved was collected in the burette. After the reaction had been brought to completion, the mixture was cooled and CH_3CN distilled off at a reduced pressure. Petroleum ether was then introduced into the flask and aqueous 10% sodium hydroxide was added slowly as hydrolyzant (in the case of methylaluminium chlorides). The methane evolved was collected in the gas burette. The petroleum ether was evaporated and the residual solution was repeatedly extracted with boiling benzene. For the determination of acetone, an aliquot of the reaction mixture was hydrolyzed with aqueous 12% hydrochloric acid.

Spectroscopy

IR spectra of complexes I in benzene solutions and of reaction products were obtained on a Zeiss UR-10 spectrophotometer. NMR spectra were recorded on a JEOL C-60H spectrometer using TMS as an internal standard.

Identification and determination of products

Acetone was identified as the 2,4-dinitrophenylhydrazone, m.p. 126-128°, and determined gravimetrically as the hydrazone.

2-Amino-3-cyano-4-imino-2-pentene, m.p. (C_6H_6) 206.5-209° (lit. [10] m.p. 206-207°); NMR spectrum (DMSO): τ −1.30, 1.31, 7.75; IR spectrum (KBr): $\nu(C\equiv N)$ 2193 cm^{-1}, ($CHCl_3$): $\nu(C\equiv N)$ 2200 cm^{-1}. (Found: C, 58.71; H, 7.17; N, 33.59. $C_6H_9N_3$ calcd.: C, 58.51; H, 7.37; N, 34.12%.) The compound was isolated from the benzenic extract of reaction products by crystallization and purified by sublimation and recrystallization from benzene. With HCl, it yields the hydrochloride. When heated in water and in aqueous sodium hydroxide, the compound hydrolyzes quantitatively to yield 2-amino-3-cyanopent-4-on-2-ene.

2-Amino-3-cyanopent-4-on-2-ene, m.p. (H_2O) 132-135° (lit. [10] m.p. 135.5-137°); IR spectrum (CCl_4): $\nu(C\equiv N)$ 2202 cm^{-1}. (Found: C, 58.28; H, 6.70; N, 22.79. $C_6H_8N_2O$ calcd.: C, 58.05; H, 6.49; N, 22.56%.) The compound was isolated from a highly diluted alkaline solution of reaction products (upon extraction with benzene). With HCl, it yields the hydrochloride. On heating in aqueous sodium hydroxide, the pentonene hydrolyzes to yield 2-hydroxy-3-cyanopent-4-on-2-ene.

2-Hydroxy-3-cyanopent-4-on-2-ene, m.p. (H_2O) 53-54° (lit. [10] m.p. 52.5-53°); IR spectrum (CCl_4): $\nu(C\equiv N)$ 2200 cm^{-1}. The compound was isolated by acidification of the alkaline aqueous solution of reaction products with hydrochloric acid (in alkaline solutions, it gives the sodium salt).

1-Cyano-2-amino-4-imino-2-pentene, m.p. (C_6H_6) 180-184°. Under the conditions of hydrolysis of the reaction mixture, the compound readily hydrolyzes to yield 1-cyano-2-amino-pent-4-on-2-ene.

1-Cyano-2-aminopent-4-on-2-ene, m.p. (H_2O) 108-112°; NMR spectrum (MeOH): τ −0.30, 3.37, 7.70; IR spectrum (KBr): $\nu(C\equiv N)$ 2220 cm^{-1}. (Found: C, 58.37; H, 6.12; N, 22.34. $C_6H_8N_2O$ calcd.: C, 58.05; H, 6.49; N, 22.56%.). The compound was isolated from the benzenic extract of reaction products by crystallization and purified by sublimation and recrystallization from water. With HCl, it yields the hydrochloride.

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