

THE REACTIONS OF TETRAALKYLALUMINOXANES WITH BENZONITRILE *

A. PIOTROWSKI, A. KUNICKI and S. PASYNKIEWICZ *

Institute of Organic Chemistry and Technology, Technical University (Politechnika), Koszykowa 75, 00-661 Warszawa (Poland)

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Summary

The reactions of benzonitrile with tetraethylaluminumoxane and with tetramethylaluminumoxane in 1 : 1 molar ratio were studied. In the case of tetraethylaluminumoxane 1,3,5-triphenyl-2,4-diaza-1-aminoheptadiene-1,4, $\text{Ph}(\text{Et})\text{HCN}=\text{C}(\text{Ph})\text{N}=\text{C}(\text{Ph})\text{NH}_2$, was found to be the main product after hydrolysis, 1,3-diphenyl-2-aza-1-aminopentene-1, $\text{Ph}(\text{Et})\text{HCN}=\text{C}(\text{Ph})\text{NH}_2$, 2,4,6-triphenylazine-1,3,5; 5-methyl-2,4,6-triphenylpyrimidine, propiophenone and benzaldehyde were also formed. A reaction scheme is proposed. In the case of $\text{Me}_4\text{Al}_2\text{O}$, acetophenone was formed as the main product after hydrolysis.

Introduction

The alkylating and reducing properties of $\text{Et}_4\text{Al}_2\text{O}$ [1] and the alkylating properties of $\text{Me}_4\text{Al}_2\text{O}$ [2] have been investigated in the reaction with 4-t-butylcyclohexanone. It was found that both compounds reacted similarly to the corresponding trialkylaluminium compounds (Me_3Al and Et_3Al). It was of interest to find how tetraalkylaluminumoxanes would react with other electron donors. We were especially interested in the reactions with benzonitrile as its complexes with $\text{Me}_4\text{Al}_2\text{O}$ and $\text{Et}_4\text{Al}_2\text{O}$ are well defined.

Results

Tetraethylaluminumoxane formed a monomeric 1 : 1 complex with benzonitrile (I) [3]. This complex underwent rearrangement upon heating at 80°C to form liquid and gaseous products. The gaseous products were analysed by

* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

TABLE 1
COMPOUNDS ISOLATED AFTER HYDROLYSIS OF THE REACTION MIXTURE

	Products	Yield ^a (%)
II	1,3,5-triphenyl-2,4-diaza-1-aminoheptadiene-1,4	40
III	1,3-diphenyl-2-aza-1-aminopentene-1	10
IV	2,4,6-triphenylazine-1,3,5	16
V	5-methyl-2,4,6-triphenylpyrimidine	
VI, VII	PhCOEt, PhCOH	5

^a The yield was calculated with respect to benzonitrile introduced.

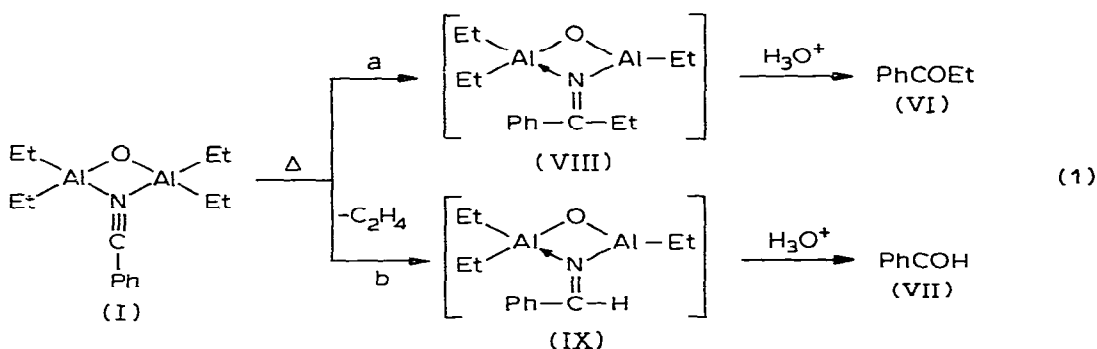
means of gas chromatography, and were found to be ethylene, ethane and ethylene oligomers. After hydrolysis of the reaction mixture several compounds were isolated (Table 1).

The above complex was also stored for 3 months at room temperature. After hydrolysis compound III was obtained in a several % yield. Compound II was not found.

Tetramethylaluminoxane formed a dimeric 1 : 1 complex with benzonitrile [4]. At elevated temperature (80°C) a rearrangement of the complex occurred yielding acetophenone (24% *) after hydrolysis. Unreacted benzonitrile was recovered (70%*).

Discussion

The monomeric complex of $\text{Et}_4\text{Al}_2\text{O}$ and PhCN underwent a rearrangement at elevated temperatures. At first alkylation (1a) or reduction (1b) of PhCN took place.

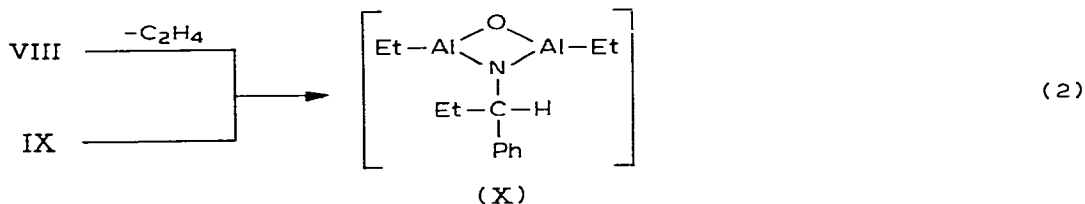


The formation of VIII and IX was confirmed by the presence of PhCOEt and PhCOH after hydrolysis of the reaction mixture (Table 1), and the presence of a band at 1640 cm^{-1} in the IR spectrum before hydrolysis. This band is attri-

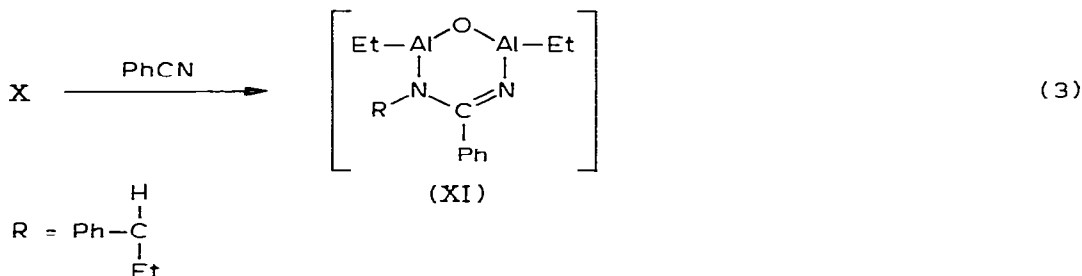
* The yield was calculated on the basis of benzonitrile introduced.

buted to the stretching vibration of the N=C bond in organoaluminium derivatives [5].

The ketimide (VIII) and aldimide (IX) derivatives underwent further reduction, or alkylation (eq. 2) due to the presence of reactive Et groups bonded to another Al atom:



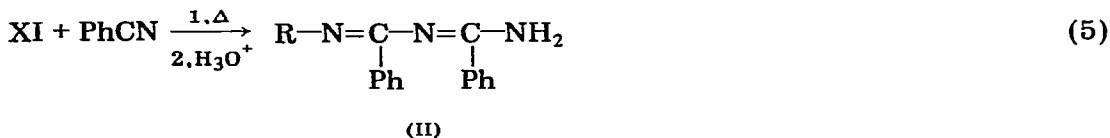
The postulated compound X reacted with benzonitrile (eq. 3) released in the thermal dissociation of complex I*.



Hydrolysis of compound XI (eq. 4) led to compound III.



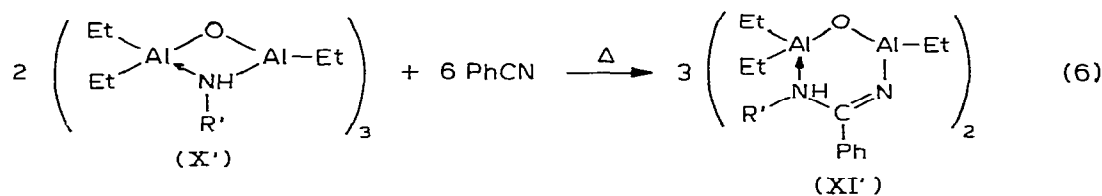
Benzonitrile inserted into the Al-N bond of compound X to give compound XI. This compound is still reactive towards benzonitrile, and a second molecule of benzonitrile was inserted (eq. 5).



Reaction 5 is dominant, because after hydrolysis only 10% of III (Table 1) was found compared with 40% of II.

To confirm the proposed reaction schemes 3 and 5 compound X' was synthesized analogously to X in a pure form [6] and reacted with benzonitrile (eq. 6).

* Evolution of free benzonitrile was observed; see experimental.

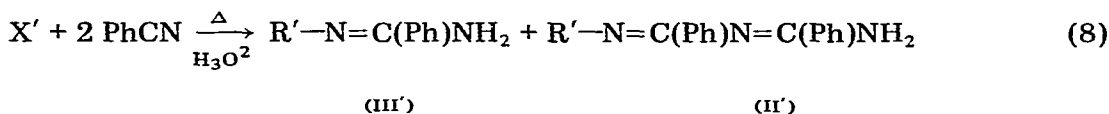


The addition reactions 6 were carried out for reactant molar ratios of 1 : 1 and 1 : 2. Reaction 6 was found to proceed readily at room temperature. According to the literature [7], addition of the Al—N bond to the C≡N group of benzonitrile takes place (see Experimental). The course of reaction 6 is identical to that postulated for reaction 3. The product XI' was isolated and hydrolysed (eq. 7).



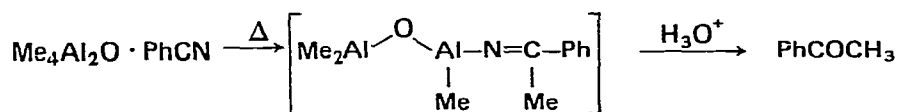
It was found that compound III' differs from compound III only, as expected, in the substituent R.

The possibility of a multiple insertion of PhCN to the Al—N bond was proved by carrying our reaction 6 for a 1 : 2 reactant ratio (eq. 8).



Compound III' was found as the main reaction product after hydrolysis. However, the presence of small amounts (a few percent) of a compound II' of molecular weight 313 was found but it was not isolated in a pure form. Its parent ion was observed in the mass spectrum of the mixture after hydrolysis. Its molecular weight is 103 greater than that of compound III'. This corresponds to addition a benzonitrile molecule to III'. The presence of the compound of molecular weight 313 indicates the possibility of a multiple insertion of the Al—N bond into the C≡N group of benzonitrile. 2,4,6-triphenyltriazine-1,3,5 (IV) and 5-methyl-2,4,6-triphenylpyrimidine (V) were formed, probably according to the scheme proposed by Kuran [8].

The reaction of tetramethylaluminum oxide with benzonitrile proceeded in a similar way as the reaction of Me₃Al with PhCN:



The reaction stopped after the formation of aluminium ketimide derivative and

upon hydrolysis acetophenone was obtained. Thus tetramethyl aluminoxane shows similar methylating properties towards benzonitrile as does Me_3Al .

Experimental

The aluminium alkyls and their derivatives, being extremely air-sensitive, were handled under dry nitrogen, or on a conventional vacuum line. Benzonitrile was purified by distillation of commercial reagent and stored over molecular sieves. Hydrocarbon solvents were dried over sodium wire, and then distilled from blue ketyl. $\text{Et}_2\text{AlOAlEt}_2$ was synthesized from the reaction of Et_3Al with water.

Measurement of physical constants

IR spectra of 5 wt-% benzene solutions were recorded on a Perkin-Elmer model 577 spectrometer. ^1H NMR spectra were recorded on a JNM-100 H Jeol spectrometer using 25 wt-% solution.

Reaction of benzonitrile with $\text{Et}_2\text{AlOAlEt}_2$

The solution of $\text{Et}_2\text{AlOAlEt}_2$ (10 mmol) in 5 cm^3 of PhCH_3 was frozen at -196°C and an equimolar amount of benzonitrile was added by distillation on a vacuum line. The mixture was warmed to room temperature and PhCH_3 was distilled off in vacuo. The reaction tube was placed in an oil bath at 110°C . Evolution of free benzonitrile was observed and a condenser was used. After 12 h, the post-reaction mixture was dissolved in 10 cm^3 of PhCH_3 and hydrolyzed with 12% HCl. The amount of propiophenone and benzaldehyde formed after hydrolysis and the unreacted benzonitrile were determined chromatographically. The amounts of the remaining products were determined approximately (by weight) after separating them by crystallization.

Reaction of benzonitrile with $\text{Me}_2\text{AlOAlMe}_2$

A solution of $\text{Me}_2\text{AlOAlMe}_2 \cdot \text{Et}_2\text{O}$ (12 mmol) in 5 cm^3 of pentane was frozen at -196°C and an equimolar amount of benzonitrile was added by distillation on a vacuum line. The mixture was warmed to room temperature. Pentane and Et_2O were distilled off in vacuo. The reaction vessel, equipped with a condenser, was placed in an oil bath at 110°C . After 12 h the post-reaction mixture was dissolved in 10 cm^3 of PhCH_3 and hydrolyzed with a mixture containing 30% HCl and 70% $\text{C}_2\text{H}_5\text{OH}$. PhCOCH_3 was determined in the form of its 2,4-dinitro-phenyl-hydrazone.

The reaction of compound X' with benzonitrile

A solution of X' (10 mmol) in 5 cm^3 of pentane was frozen at -196°C and an equimolar amount of benzonitrile was added by distillation on a vacuum line. The mixture was warmed to room temperature. Pentane was then distilled off in vacuo. The reaction tube was placed in an oil bath at 110°C .

The reaction course was observed by recording IR spectra of the reaction mixture 15 minutes after mixing the reactants (Fig. 1a) and after completion of the reaction (Fig. 1b). In spectrum 1a characteristic bands for compound X' and benzonitrile are present. The band at 3268 cm^{-1} corresponds to stretching

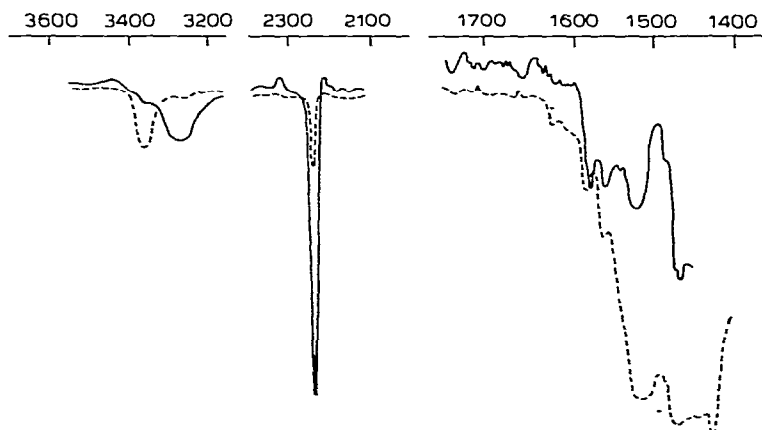


Fig. 1. IR spectra; (-----) reaction mixture 15 minutes after mixing the reactants; (——) reaction mixture after completion of the reaction.

vibrations of the N—H bond of compound X'. The band at 2230 cm^{-1} corresponds to stretching vibrations of the benzonitrile $\text{C}\equiv\text{N}$ group. This band does not show a shift towards higher frequencies, which is characteristic for nitrile complexes. After completion of the reaction the band at 3268 cm^{-1} shifts by about 100 cm^{-1} to 3360 cm^{-1} . The band at 2230 cm^{-1} of nitrile disappears and a new band appears at 1538 cm^{-1} , attributable to the vibrations of the $\text{N}=\text{C}-\text{N}$ system.

These facts prove the addition of the Al—N bond to the $\text{C}\equiv\text{N}$ group of benzonitrile.

Compound XI' was isolated from the post-reaction mixture by multiple precipitation from a pentane solution at reduced temperature.

Analysis: found Al, 14.20; Et, 24.0, $\text{C}_{20}\text{H}_{28}\text{Al}_2\text{N}_2\text{O}$ Calc.: Al, 14.73; Et, 23.79%.

Cryoscopic molecular weight determination in benzene showed that compound XI' is a dimer in solution. In order to determine the structure of this compound, its ^1H NMR and ^{13}C NMR spectra were recorded.

A broad signal at 0.0 ppm is present in the ^{13}C NMR spectrum of XI' (Fig. 2). It is derived from α carbons of ethyl groups bonded to aluminium. The β carbons appear as three signals at 9.69, 9.86 and 10.09 ppm. At 46.73 and 51.72 ppm the signals of the benzyl group methylene carbons are present. The signals at 112.78 and 118.69 ppm are difficult to identify. Most probably they are the signals of carbons of the $\text{N}=\text{C}-\text{N}$ groups. The signals of aromatic carbons are overlapped by the solvent signal (benzene).

From the spectrum it appears that of ethyl groups bonded to aluminium exist in the dimer of compound XI' (at least three such groups) and at least two different benzyl groups. The ^1H NMR spectrum (Fig. 3) confirms these observations.

In the ^1H NMR spectrum of XI' (Fig. 3), in the range expected for protons of ethyl groups bonded to aluminium a complex multiplet at 9.55 ppm, corresponding to the CH_2 group, and a multiplet of the CH_3 group at 8.90 ppm are

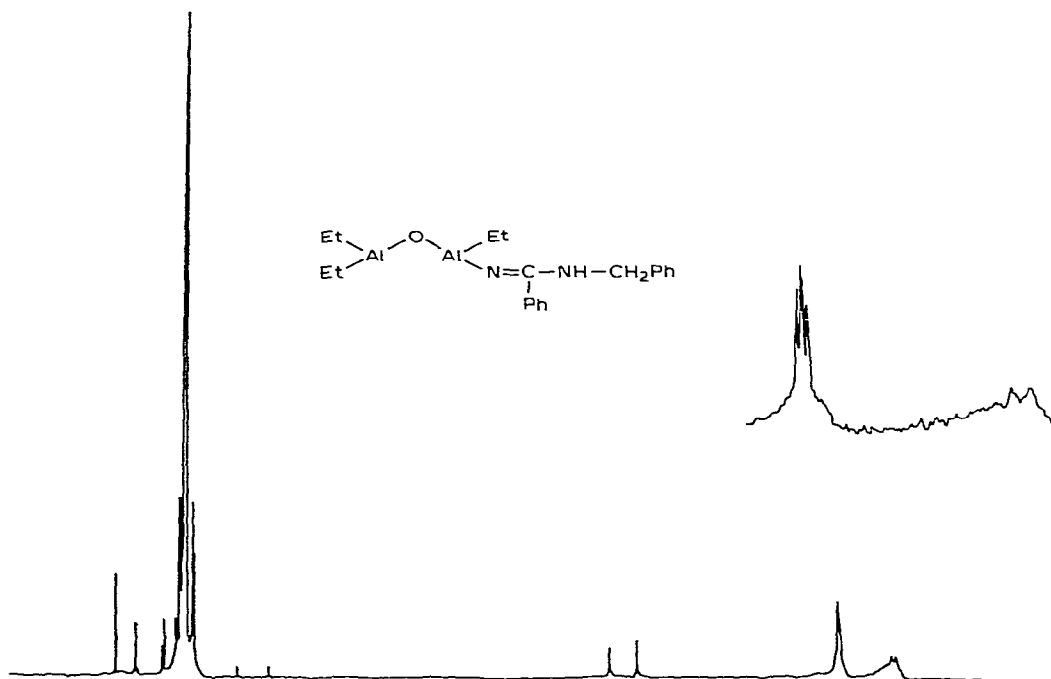


Fig. 2. Carbon ^{13}C NMR spectrum of compound XI'.

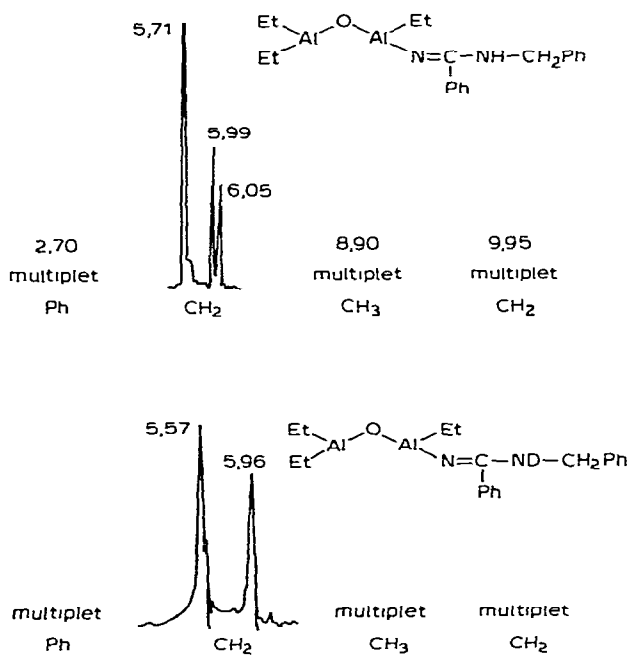
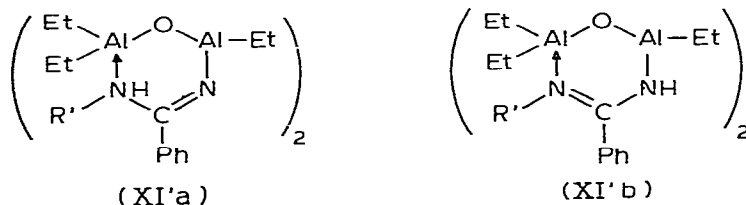


Fig. 3. The proton NMR spectrum of compound XI' and deuterated compound XI'.

present. In the range expected for protons of the benzyl methylene groups three signals are present: a singlet at 5.71 ppm and a doublet at 6.02 ppm. The complex multiplet at 2.70 ppm corresponds to the signals of aromatic protons. It was found that the doublet at 6.02 ppm was a spin doublet $J(\text{NH}-\text{CH}_2) = 6.37$ Hz, since in the spectrum of the N-deuterated compound (Fig. 3b) a singlet was observed in the place of the doublet.

In the ^{13}C NMR and ^1H NMR spectra of compound XI' two different benzyl groups are observed. They differ not only in chemical shifts but also in coupling constants $J(\text{NH}-\text{CH}_2)$, which are equal to 6.37 and 0 Hz, respectively. This indicates the presence of two tautomers XI'a and XI'b.



Compound III' was identified by its elemental analysis (found: C, 68.15; H, 6.08; N, 11.29 $\text{C}_{14}\text{H}_{14}\text{N}_2$ calc.: C, 68.15; H, 6.13; N, 11.35%) and analysis of their mass spectrum.

The identification and analyses of the products: 1,3-diphenyl-2-aza-1-aminopentene-1 NMR (CD_3OD) $\tau = 9.00$ (triplet, CH_3); 8.16 (sextet, CH_2); 5.50 (triplet, CH); 2.60 (Multiplet, Ph). IR (CHCl_3): 3440m, 3400m ($\nu(\text{NH}_2)$); 1642vs ($\nu(\text{C}=\text{N})$). Mass spectrum 70 ev: m/e 238 (Parent Ion); 237 ($M - \text{H}$); 209 ($M - \text{Et}$); 106 (m/e 209 - PhCN); 104, 103 (PhCN). Elemental analysis found C, 80.01; H, 7.48; N, 11.60 $\text{C}_{16}\text{H}_{18}\text{N}_2$ calcd.: C, 80.63; H, 7.61; N, 11.75%. 1,3,5-triphenyl-2,4-diaza-1-aminoheptadiene-1,4. This compound was identified by analysing the mass spectra of its hydrochloride and trimethyl iodide salts. 2,4,6-triphenylazine-1,3,5 and 5-methyl-2,4,6-triphenylpyrimidine.

These compounds were identified by the analysis of their mass spectra.

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