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# REACTIONS OF METHYLALUMINIUM COMPOUNDS WITH METHACRYLONITRILE

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## SUMMARY

Reactions of trimethylaluminium, dimethylaluminium chloride and methylaluminium dichloride with methacrylonitrile have been investigated. These reactions afford corresponding donor–acceptor complexes. At elevated temperatures they react to yield methyl isopropenyl ketone (upon hydrolysis) and oligomers. During these reactions methane is formed in small amounts. The yield of reaction products has been studied in relation to the nature of methylaluminium compound and the reaction temperature.

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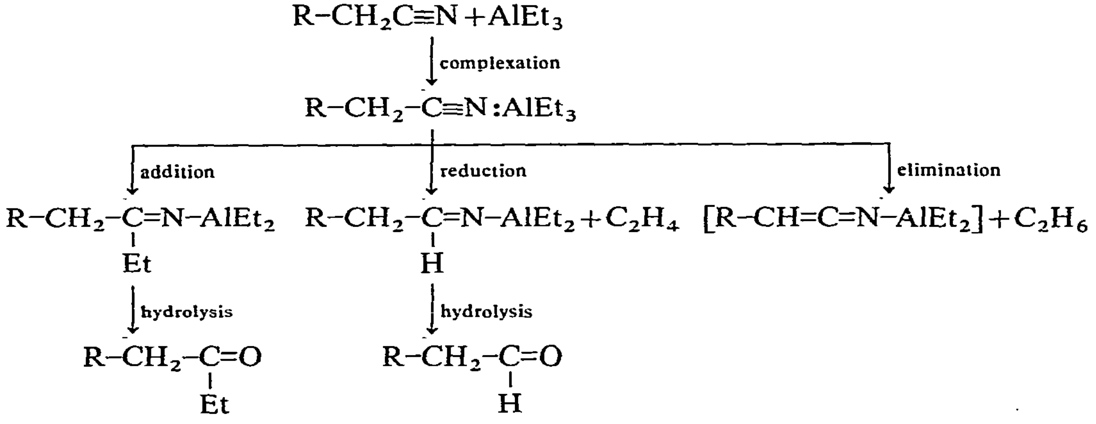
The reactions of organoaluminium compounds with the nitriles of saturated aliphatic acids and aromatic acids have been studied[1]. According to the types of nitrile and the organoaluminium compound, these reactions can proceed in several directions comprising of addition, reduction, and elimination, as illustrated by the following scheme:



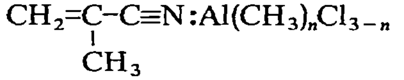
All nitriles are capable of entering the addition and reduction reactions but elimination reaction is feasible only with the nitriles having a mobile hydrogen atom α to the nitrile group.

In the reactions of acrylonitrile with methylaluminium compounds methane is evolved and dihydro- and hexahydropyrimidine derivatives are produced[1]. Methyl vinyl ketone is not formed whatsoever, a fact indicating that in this case the addition reaction (feasible with all other nitriles) does not proceed. Acrylonitrile reacts analogously with ethylaluminium compounds to yield ethane and corresponding hydropyrimidine derivatives. Ethylene is also produced and compounds are formed which contain carbonyl groups (upon hydrolysis)[2]. These products are formed via the elimination route which complexes of acrylonitrile and ethylaluminium compounds are likely to follow. Bogdanovič and Velič[3] obtained an analogous derivative by reacting acrylonitrile with diisobutylaluminium hydride, *viz.*, $CH_2{=}CH{-}CH{=}N{-}Al(i\text{-}Bu)_2$.

The purpose of the present study is to explore the reactions of methylaluminium compounds with methacrylonitrile. Unlike acrylonitrile, it has no hydrogen atom at the carbon in position $\alpha$ to the nitrile group.

## RESULTS AND DISCUSSION

Reactions of methacrylonitrile with trimethylaluminium, dimethylaluminium chloride and methylaluminium dichloride were investigated. Likewise other nitriles, methacrylonitrile forms donor–acceptor complexes (I) with these methylaluminium compounds, *viz.*,

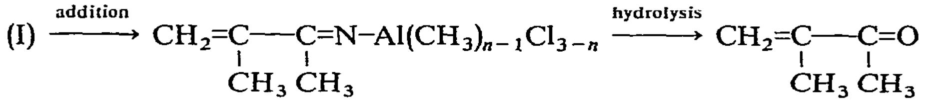


$$CH_2{=}\underset{CH_3}{C}{-}C{\equiv}N{:}Al(CH_3)_nCl_{3-n} \qquad (I)$$

where $n=1, 2, 3$.

Infrared studies disclosed that the 2231 $cm^{-1}$ band characteristic of the nitrile group in the free methacrylonitrile is, in the complexes (I) of methacrylonitrile with trimethylaluminium, dimethylaluminium chloride and methylaluminium dichloride shifted to 2274, 2279 and 2285 $cm^{-1}$, respectively.

The resulting complexes (I) of methacrylonitrile and the methylaluminium compounds undergo the addition reaction to produce ketone (eqn. 1):



$$(I) \xrightarrow{\text{addition}} CH_2{=}\underset{CH_3}{C}{-}\underset{CH_3}{C}{=}N{-}Al(CH_3)_{n-1}Cl_{3-n} \xrightarrow{\text{hydrolysis}} CH_2{=}\underset{CH_3}{C}{-}\underset{CH_3}{C}{=}O \qquad (1)$$

where $n=1, 2, 3$.

The yields of methyl isopropenyl ketone formed in the reactions (1) are listed in the Table. These are in the order $MeAlCl_2 < Me_2AlCl < Me_3Al$ for the complexes (I). With the reactants used in the mole ratio 1/1 at a temperature of 150°, and the reaction time of 3 h, the yields of the ketones obtained with trimethylaluminium, dimethylaluminium chloride, and methylaluminium dichloride are 19.9, 3.2, and 0.5%, respectively (Table 1). The yield of the ketone increases as the mole ratio of the methylaluminium compound to methacrylonitrile is increased from 1/1 to 2/1.

The data obtained indicate that the addition (1) involves migration of the methyl group endowed with an electron pair from the aluminium atom to the carbon atom of the nitrile group (in either the four- or the six-centre system according to

TABLE 1

YIELDS OF PRODUCTS OF THE REACTION BETWEEN METHACRYLONITRILE AND METHYLALUMINIUM COMPOUNDS

| $Me_nAlCl_{3-n}$ (mmoles) | $Me_nAlCl_{3-n}$ $CH_2{=}C(CH_3)CN$ | Temp. (°C) | Time (h) | Yield[a] (%) | | | Methyl groups reacting (%)[a] |
|---|---|---|---|---|---|---|---|
| | | | | Ketone | Oligomers | Methane | |
| *$Me_3Al$* | | | | | | | |
| 12.5 | 1/1 | 120 | 3 | 6.9 | 42.3 | 3.3 | |
| 12.0 | 1/1 | 120 | 9 | 10.4 | 52.6 | 6.3 | |
| 29.2 | 2/1 | 120 | 3 | 13.7 | 36.5 | 2.9 | |
| 12.5 | 1/1 | 150 | 3 | 19.9 | 71.6 | 5.4 | 28.0 |
| 12.5 | 1/1 | 170 | 3 | 10.2 | 75.0 | 6.4 | 52.0 |
| *$Me_2AlCl$* | | | | | | | |
| 12.4 | 1/1 | 120 | 3 | 1.2 | 54.0 | 2.4 | 9.6 |
| 11.8 | 1/1 | 120 | 9 | | 80.0 | 11.0 | 22.8 |
| 32.1 | 2/1 | 120 | 9 | 3.4 | 36.8 | 6.8 | 26.4 |
| 11.9 | 1/1 | 150 | 3 | 3.2 | 79.3 | 16.8 | |
| *$MeAlCl_2$* | | | | | | | |
| 14.6 | 1/1 | 120 | 3 | | | 0.1 | 2.7 |
| 31.0 | 1/1 | 120 | 9 | | 3.5 | 1.6 | |
| 7.7 | 1/1 | 150 | 3 | 0.5 | 8.4 | 1.6 | 9.7 |
| 23.8 | 1/1 | 170 | 9 | 2.9 | 55.2 | | |
| 23.7 | 2/1 | 170 | 9 | 5.3 | 14.1 | 14.0 | 21.8 |

[a] Based on the methacrylonitrile/methylaluminium compound complexes (per single methyl group).

the mole ratio used)[4]. With the methacrylonitrile complex as reactant the addition (1) yield is much lower than the yields obtained with the complexes of saturated acid nitriles. For example, with an equimolecular complex of tert-butyl cyanide and trimethylaluminium allowed to react for 3 h at 150° the methyl tert-butyl ketone was obtained in 95% yield[5]; on the other hand, with the methacrylonitrile/trimethylaluminium complex the methyl isopropenyl ketone yield was 19.9% only. The low yield of methyl isopropenyl ketone is due to the presence of a double bond in methacrylonitrile. Owing to the effect of coupling with the nitrile group, the $\pi$-electrons of this bond give rise to a reduction of the partial positive charge on the carbon atom of this group. In the molecule of the complex of a saturated acid nitrile like tert-butyl cyanide, the analogous charge is higher. The higher is the partial positive charge, easier the addition reaction[6].

In addition to methyl isopropenyl ketone, the reactions of methacrylonitrile with methylaluminium compounds afford solid products (80%) and small amounts of methane (Table 1). In the present study, these were not identified. When followed in terms of IR spectra of the reaction mixture, the reaction was found to be accompanied by progressive disappearance of the bands characteristic of the complexed nitrile group and intensification of absorption bands within the range 1620–1660 cm$^{-1}$ (C=C and C=N stretching vibrations). After hydrolysis of the solid products and removal of methyl isopropenyl ketone and unconverted methacrylonitrile, the IR spectra revealed the presence of very intense bands near 1600 cm$^{-1}$ and a weak band (2230 cm$^{-1}$) characteristic of the nitrile group but no bands attributable to carbonyl groups. The solid products are soluble in benzene, acetone, and aqueous mineral acids. On heating with aqueous 20% sodium hydroxide, these hydrolyze to yield ammonia and, among other things, salts of organic acids which were not identified.

The solid products are probably formed primarily by oligomerization of complexes (I) via the nitrile groups with the formation of C=N bonds. As is evident from our studies, the amount of the methyl groups derived from the methylaluminium compound, which undergo reaction, is greater than that demanded by the addition equation (1) and accounted for by the methane evolved. This fact indicates that in the resulting oligomers the methyl groups continue to react. The Table lists the over-all amounts of reaction of the methyl groups in the reactions of methacrylonitrile with the methylaluminium compounds, as calculated from the volume of methane liberated on hydrolysis of the products. The products of addition (1) (ketimine derivatives) do not undergo polymerization, because no carbonyl groups were found to be present in the solid products (upon hydrolysis).

Comparisons of the courses and products of the reactions of methacrylonitrile and acrylonitrile with methylaluminium compounds show that, unlike the acrylonitrile reactions, in the methacrylonitrile reactions the formation of solid products (oligomers) is not related to the reaction of elimination of methane. In these reactions the evolution of methane proceeds only with difficulty and may be due to thermolysis of the organoaluminium compound (particularly at elevated temperatures and prolonged reaction times). Nor can be ruled out as a possibility the formation of methane by interaction of the methyl groups at the aluminium atom with the hydrogen atoms of the methyl group at the carbon atom. With the methacrylonitrile complex (I) as reactant, oligomers also form with difficulty and therefore a competitive reaction of addition (1), affording ketone, may take place. This reaction is impeded, however, owing to the reduction of the partial positive charge on the carbon atom of the nitrile group on account of the presence of double bond in the molecule.

On the other hand, in the reactions of acrylonitrile with methylaluminium compounds the elimination of methane, combined with trimerization, proceeds very easily, thereby rendering the ketone-producing addition impossible.

## EXPERIMENTAL

The preparation of materials, apparatus, and procedures employed in studying the reactions of methacrylonitrile with methylaluminium compounds were the same as those described earlier for the reactions of acrylonitrile with these compounds[1]. Methacrylamide-free methacrylonitrile was used in the reactions. The reaction mixture was hydrolyzed with a (1/3 by vol.) mixture of concentrated hydrochloric acid and methanol containing (0.5% by wt.) hydroquinone. Once hydrolyzed, the contents of the reactant passed went into solution.

Methyl isopropenyl ketone was identified and analyzed as the 2,4-dinitrophenylhydrazone (m.p. 189° upon recrystallization from methanol).

Oligomers (occurring as hydrochlorides in the solution) were isolated by diluting the solution with water, adding alkali and extracting the resulting solution repeatedly with benzene. The benzene, ketone, and possibly unconverted methacrylonitrile were evaporated from the extract. The products thus isolated were not purified. The elemental analysis revealed the presence of nitrogen.

Infrared studies on methacrylonitrile and its complexes with methylaluminium compounds and on samples of the reaction mixture were performed in benzene solutions. Prior to hydrolysis, the products of the reactions of methacrylonitrile with the methylaluminium compounds were run as Nujol mulls; the hydrolyzates were studied as benzene solutions.

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