

# REACTIONS OF ORGANOALUMINIUM COMPOUNDS WITH ELECTRON DONORS

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## ABSTRACT

The application of organoaluminium compounds as components of organo-metallic or complex systems is connected with a knowledge of their reactions with electron donors. Reactions with nitriles, ketones, esters, ethers, alkyl chlorides, vinyl chloride, and acid chlorides as the electron donors were investigated.

The first stage of the reaction of an organoaluminium compound with an electron donor involves formation of the corresponding donor-acceptor complex. A knowledge of the structure of the formed complexes is very important for an elucidation of the reaction course and mechanism. The heat of formation, composition, and molecular weight of the corresponding complexes were determined, and their i.r. and n.m.r. spectra were studied.

From these investigations general conclusions were made concerning, the influence of the Lewis acidity of the organoaluminium compound on the structure of its complexes and on their reactivity; the effect of reactant mole ratio (organoaluminium compound to electron donor) on the reaction course, and the influence of the molecular structure of the complex and of dislocation of electrons on the reaction mechanism.

Hallwachs and Schafarik<sup>1</sup> synthesized the first organoaluminium compound 120 years ago. By treating aluminium with ethyl iodide they prepared ethylaluminium sesqui-iodide. However, the chemistry of organo-aluminium compounds received little attention until the investigations of Ziegler and his collaborators, in about 1950.

The development of the direct synthesis of organoaluminium compounds from aluminium, ethylene, and hydrogen, and elaboration of normal pressure polymerization of ethylene, aroused great interest. Almost simultaneously, numerous research centres over the world undertook research and technological investigations.

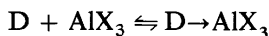
Organoaluminium compounds proved to be of both theoretical and technological interest because of their ability to form auto and other complexes, their high reactivity, and associated structure and valence theory problems.

In spite of the two decades that have passed since Ziegler's discoveries and the intensive studies that have been conducted throughout, the interest in the chemistry of organoaluminium compounds has not declined. This is mainly due to the use of organoaluminium compounds as constituents of complex catalyst systems.

Such systems have been broadly employed in a number of processes including poly-, co-, and oligomerization, alkylation, carbonylation, reduction, and like processes. Often of prime significance in preparing active catalyst systems is the use of an electron donor which is employed as a solvent or an indispensable activator. Therefore, a knowledge of the reactions of organoaluminium compounds with electron donors may contribute to the elucidation of the nature of catalyst systems and the mechanism of catalysis.

The present paper sets out to review the reactions of organoaluminium compounds with organic electron donors.

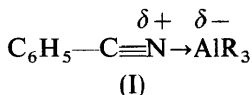
The aluminium atom has free 3p and 3d-orbitals characterized by fairly low energies. They permit ready formation of complexes with electron donors. A first stage of the reaction of an organoaluminium compound with an electron donor involves formation of a complex, which is often stable enough to be separated and finely examined. Thus far complexes of organoaluminium compounds with nitriles<sup>2-5</sup>, ethers, and esters have been prepared. Complexes with ketones, alkyl chlorides, and acid chlorides have also been postulated. Schematically the formation of a complex may be represented as follows



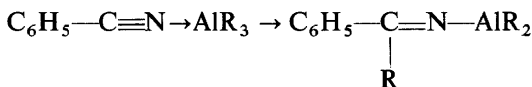
where D = electron donor and X = alkyl, aryl, halogen, etc.

At suitable temperatures the complex will enter into further reactions. These may include addition, reduction, elimination, insertion, and cyclization. It should be emphasized that with electron donors such as nitriles, ketones, esters, ethers, etc., organoaluminium compounds react in similar fashions and according to like mechanisms. This fact enables some general conclusions to be drawn, the recognition of which may facilitate studies of new reactions.

Let us begin by reviewing the reactions of organoaluminium compounds with nitriles as electron donors. These reactions afford 1:1 complexes<sup>2-5</sup> which are stable at room temperature, linear in structure, and which may be represented as follows

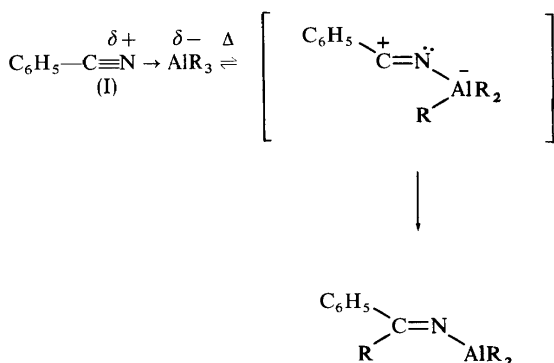


At elevated temperature the complex (I) undergoes an addition reaction to yield an aluminium ketimine derivative



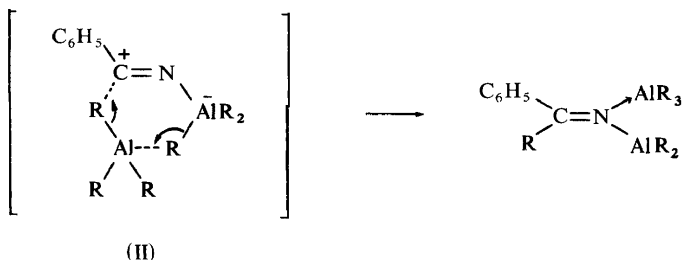
The addition of trimethylaluminium to benzonitrile<sup>6-7</sup> has been investigated extensively. The reaction rate was found to depend on the mole ratio of the reactants. At the ratio of 1:2 (excess of Me<sub>3</sub>Al), the addition proceeds at a faster rate than an equimolar reaction. This is explained in terms of the reaction mechanism.

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Owing to a change in hybridization of the nitrogen atom from  $sp$  to  $sp^2$ , the linear complex (I) alters its geometrical structure at elevated temperatures. The R group closely approaches the positively charged carbon atom in the nitrile group, and this may eventually result in R, together with an electron pair, being intramolecularly rearranged from the aluminium atom to the carbon atom.

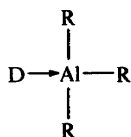
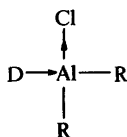
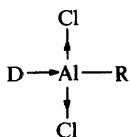
With the reactants used in the mole ratio 1:2, an intermediate complex (II) is formed:



In this complex, because it is a six-centre system, the R group moves extremely close to the carbon atom of the nitrile group. It is this fact that explains why the 1:2 addition proceeds faster than the 1:1 addition.

The above rule relating the rate of addition to the mole ratio of reactants holds true for other electron donors.

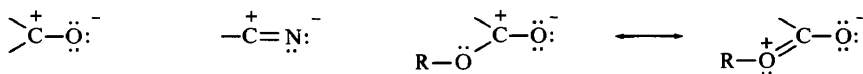
In addition to the effect of reactant mole ratio on the addition rate, the type of organoaluminium compound is also of consequence. The type of compound highly affects the yield of addition. The mechanism of the reaction remains unaffected, however. The addition yield was studied in relation to the type of methylaluminium compound in its reactions with benzonitrile<sup>8</sup>, methacrylonitrile<sup>9</sup>, and benzyl cyanide<sup>10</sup>. In these reactions the yield of addition was found to increase in the order,  $\text{RAlCl}_2 < \text{R}_2\text{AlCl} < \text{R}_3\text{Al}$ , that is, to be related to the acid strength of the organoaluminium compound. This dependence is obviously associated with the fact that, if the organoaluminium compound is a weak Lewis acid, the R group and its electron pair can be easily abstracted from the aluminium atom.



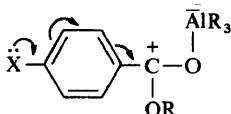
Conversely, if the organoaluminium compound is a strong acid (extraction of electrons by the chlorine atoms), abstraction of the  $\text{R}^-$  group is difficult and addition proceeds with low yield.

The relevant rule may be formulated as follows: the addition reaction proceeds more readily, the weaker the acidity of the organoaluminium compound. This rule holds true for one type of electron donor. With various donors, the addition reaction proceeds more easily, the stronger the basicity of the donor. The base strength renders abstraction of the  $\text{R}^-$  group from the aluminium atom easier, and thus facilitates addition.

In the active complex of an organoaluminium compound with an electron donor, addition proceeds more easily, the larger the positive charge on the nitrile or the carbonyl carbon atom. The following formulae representing the ketone, nitrile, and ester demonstrate that the largest positive charge occurs in the ketone:



The charge on the nitrile carbon atom is reduced because of partial compensation by the carbon–nitrogen double bond. Similarly, the positive charge on the carbonyl carbon atom in the ester molecule is considerably reduced by a shift of electrons from the OR group towards this carbon atom. Investigations into the effect of positive charge on the yield of addition have been carried out in the reactions of *para*-substituted esters with triethylaluminium<sup>11</sup>. With various substituents X the geometrical structure of, and the steric hindrance in the compound are unaffected and only the electrophilicity of the carbonyl carbon atom varies

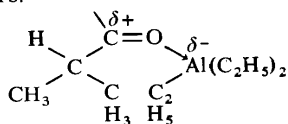


Electron-donating substituents reduce the positive charge on the carbon atom and thus render rearrangement difficult. Electron-accepting substituents have the opposite effect. The yield of reaction is closely dependent on the substituent type and varies fourfold as the substituent is changed from  $\text{OCH}_3$  to  $\text{CN}$ . The conclusion to be drawn is that the positive charge on the carbon atom to which the R group migrates, is favourable to this rearrangement.

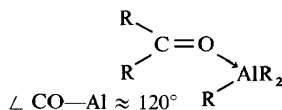
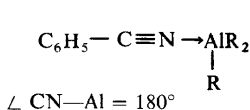
Another significant factor operative in addition is the spatial structure of the complex. For the rearrangement to proceed easily the R group must approach the carbon atom. When steric hindrance renders this approach difficult, no addition occurs. This is the case with diisopropyl ketone and triethylaluminium<sup>12</sup>. The two bulky isopropyl groups render the requisite

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approach of the ethyl group to the carbonyl carbon atom impracticable, and thus no addition occurs.



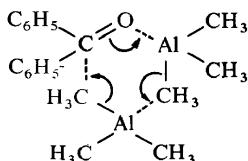
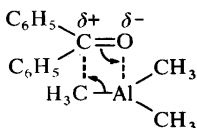
The angle between the active carbon atom and the aluminium atom in the resulting complex is also of consequence. If the angle is  $180^\circ$ , as is the case with nitrile complexes, rearrangement is difficult because the R group is a considerable distance from the nitrile group carbon atom. When the angle is less than  $180^\circ$ ,



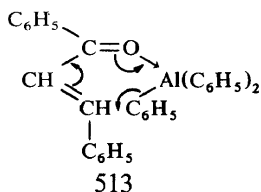
as is the case, e.g. with ketones, rearrangement is feasible.

The yield of addition, in relation to the type of substituent at the aluminium atom, has not been thoroughly investigated. However, the existing data<sup>8</sup> indicate that the substituents can be arranged in the following order of decreasing activities: methyl > ethyl > phenyl.

With electron donors other than nitriles, addition proceeds in a similar fashion. A mechanism for the addition of organoaluminium compounds to ketones has been suggested on the basis of chemical investigations<sup>12, 14</sup>. The kinetic investigations of Ashby *et al.*<sup>15, 16</sup> bore out this mechanism. With benzophenone and trimethylaluminium, used at mole ratios of 1:1 and 1:2, rearrangements occur in the four-centre and the six-centre systems, respectively.

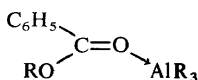


As with nitriles, the addition reactions with ketones are affected by the mole ratio of reactants<sup>14, 15</sup>, the acid strength of the organoaluminium compound<sup>12</sup>, the size of the positive charge on the carbonyl group, and the steric configuration of the reacting complex<sup>12</sup>. All the rules formulated for nitriles are valid for ketones. The reaction of triphenylaluminium with an  $\alpha, \beta$ -unsaturated ketone<sup>17</sup> illustrates the role of the positive charge on the carbon atom to which the aluminium-borne substituent becomes rearranged, and the distance of this substituent from the positively-charged carbon atom.



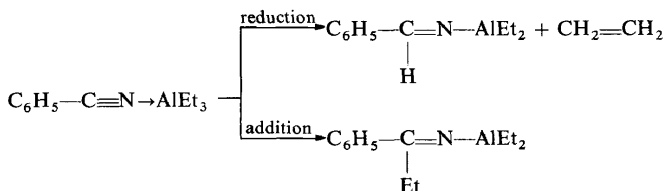
In this case, 1,4-addition occurs exclusively because both the larger positive charge on the  $\beta$ -carbon atom and the lesser distance of the phenyl group from the  $\beta$ -carbon atom are conducive to this type of addition.

Esters react readily with organoaluminium compounds to yield donor-acceptor complexes at room temperature. Infrared absorption spectra<sup>18</sup>, molecular weight determinations, and elemental analyses<sup>19</sup>, show that the 1:1 complexes are formed with the aluminium atom attached to the carbonyl group.



Such complexes are slightly reactive and on hydrolysis revert to the esters. The main reason for the slight reactivity of the complex is the small positive charge accumulated on the carbonyl carbon atom. This charge has been considerably reduced by interaction with the free electron pairs on the alkoxy group oxygen. However, at elevated temperatures addition does occur. The yield is low<sup>11</sup> on account of subsequent reactions<sup>20, 21</sup> which afford secondary and ternary alcohols and other products according to the type of ester and organoaluminium compound used.

Ethyl- and higher alkylaluminium compounds react with electron donors to yield not only addition but also reduction products. The reaction of benzonitrile with triethylaluminium affords products of addition and reduction<sup>13</sup>.



With a given organoaluminium compound, the ratio of the amounts of reduction to addition is governed primarily by the mole ratio of reactants. As is evident from *Figure 1*, the yields of reduction and addition are closely

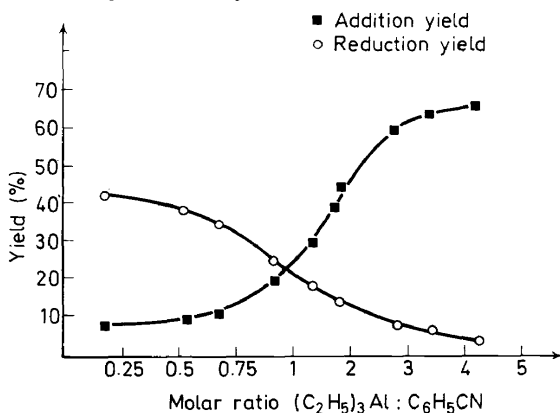
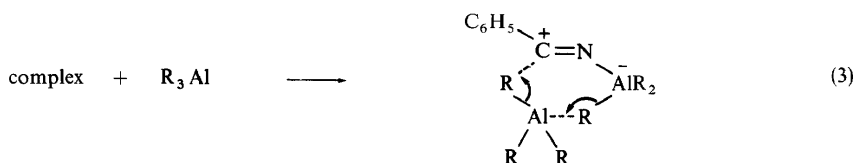
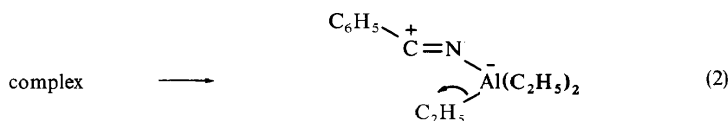
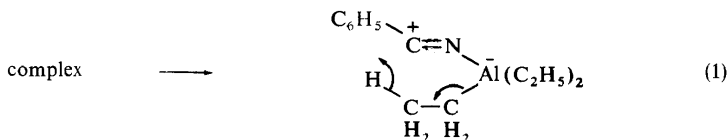


Figure 1

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dependent on the ratio of triethylaluminium to benzonitrile. When the latter is used in fourfold excess over the former, reduction predominates; at the opposite excess, addition prevails. The mechanisms of addition and reduction explain the above behaviour.



Reaction (3) proceeds much faster than reactions (1) and (2)<sup>13, 22</sup>. As already indicated, this is due to the favourable six-centre system. Such a system is formed most easily when the organoaluminium compound is used in excess. With excess benzonitrile reaction (1) proceeds more readily than reaction (2) and therefore the reduction product is the major component of the reaction mixture.

Temperature greatly affects the direction of the benzonitrile-triethylaluminium reaction. At 80°C, the reduction is non-existent; at 150°C, moderate (20 per cent)<sup>13</sup>, and at 190–200°C, predominant<sup>5</sup>.

As with nitriles, the yields of reduction and addition reactions with ketones are affected by the mole ratio of reactants. An excess of triethylaluminium over diethyl ketone<sup>12</sup> is conducive to addition (cf. Figure 2).

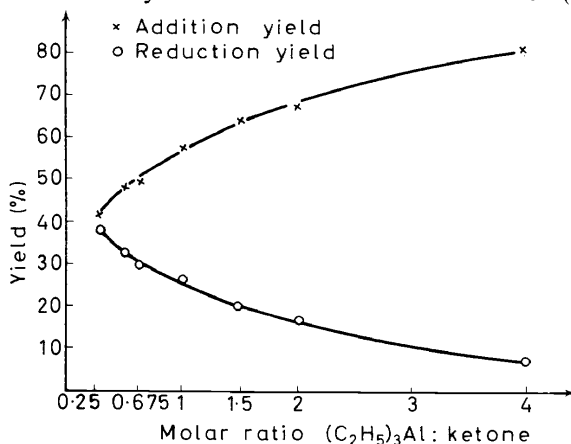
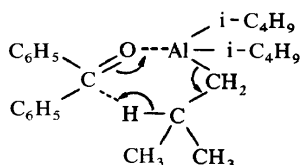


Figure 2

The yield of reduction is related to the acid strength of the organoaluminium compound. The weaker the acidity of this compound, the more readily the reduction proceeds. With diisopropyl ketone and triethylaluminium, used mole per mole at 65°C, the yield of reduction is 86 per cent; with diethylaluminium chloride the yield is 37 per cent, and with ethylaluminium dichloride the reaction fails to occur<sup>12</sup>.

Higher alkylaluminium derivatives reduce electron donors more readily than ethylaluminium derivatives. With triisopropylaluminium and triisobutylaluminium, reduction occurs and addition is non-existent. The two underlying reasons are: (i) the bulky isopropyl and isobutyl groups prevent approach to the positively-charged carbon atom of the carbonyl or the nitrile group and (ii) hyperconjugation of the methyl group facilitates elimination of the hydride ion.

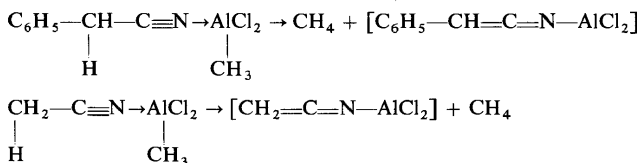
The mechanism of reduction of benzophenone by triisobutylaluminium was proved by Ashby<sup>23</sup>. The reduction proceeds in the six-centre system by an attack of  $\beta$ -hydrogen on the carbonyl group.



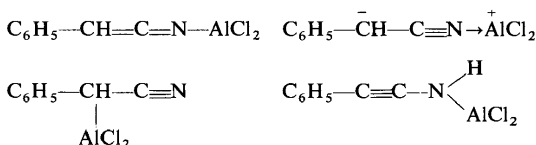
In this case, excess of the organoaluminium compound is of no significance because with the bulky isobutyl group addition is not feasible.

The elimination reaction has received less attention than the addition and reduction reactions. Elimination proceeds with organoaluminium compounds and electron donors having a mobile hydrogen atom, or a group easily eliminated as a cation.

Phenylacetoneitrile and acetonitrile have mobile hydrogen atoms  $\alpha$  to the nitrile group and therefore can react with an appropriate organoaluminium compound to eliminate methane



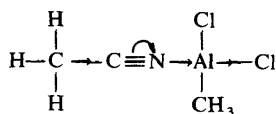
As a result, an unstable compound is formed which immediately enters into a subsequent reaction with the nitrile present in the reaction mixture. This intermediate compound has not yet been examined and a variety of formulae may be ascribed to it. e.g.





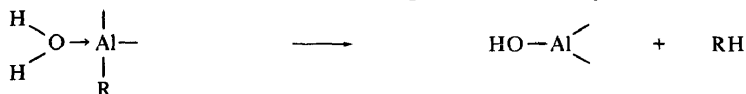
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The rate of elimination can be followed by measuring the reaction time and the volume of methane evolved. This rate has been shown to depend primarily on the acid strength of the organoaluminium compound<sup>16</sup>. For phenylacetonitrile<sup>24</sup> and acetonitrile<sup>25</sup>, elimination rates rise in the sequence.  $R_3Al < R_2AlCl < RAlCl_2$ . It should be mentioned that in elimination reactions the order of reactivity of the organoaluminium compounds is the reverse of that observed in the addition and reduction reactions. This fact indicates that the elimination reaction follows a different mechanism. The most reactive organoaluminium is a strong Lewis acid, which shows that elimination of a methyl group from the aluminium atom is not rate-controlling. The strong acid extracts electrons causing the  $\alpha$ -hydrogen to become more mobile.

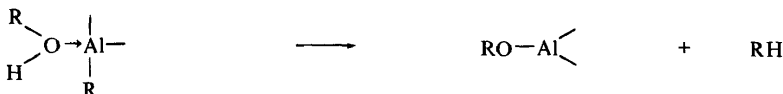


For a given donor the acid strength of the organoaluminium compound used affects the mobility of the hydrogen atom: the more mobile the hydrogen, the more easy the elimination.

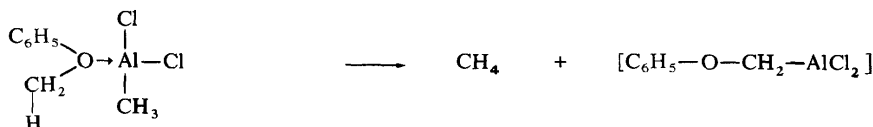
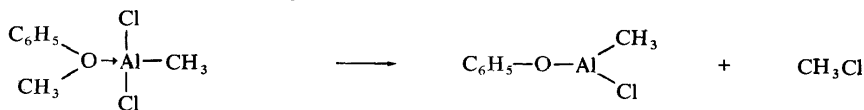
For a given organoaluminium compound, the mobility of the hydrogen atom in the donor molecule controls the rate of elimination. Water, as an electron donor, has such a mobile hydrogen that the elimination reactions with lower organoaluminium compounds proceed violently.



Alcohols react much less rapidly owing to the lesser mobility of their hydrogen atoms.

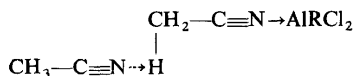


In both of these reactions the acid strength of the organoaluminium compound has only a slight effect on the over-all reaction rate. However, with ethers<sup>26</sup> and esters<sup>27</sup> the acid strength of the organoaluminium compound has a considerable effect on the elimination rate. In addition to methane, ethers and esters eliminate alkyl chlorides. With anisole, elimination of methyl chloride is the major reaction:

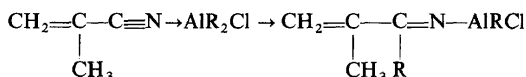


In elimination reactions the mole ratio of the reactants is of major importance. This is clearly evident from the reactions of slightly reactive nitriles. Acetonitrile on reaction with methylaluminium dichloride<sup>25</sup>, mole ratio 2:1, eliminates methane in nearly 100 per cent yield at 120°C; at the 1:1 ratio, the reaction proceeds only at 170°C; and at the 1:2 ratio (MeAlCl<sub>2</sub> in excess), the reaction does not occur. Phenylacetonitrile<sup>24</sup> has revealed a similar behaviour.

The above data indicate that an excess of the nitrile facilitates and promotes elimination, whereas an excess of the organoaluminium compound has an opposite effect. The role of the excess nitrile may be explained by solvation. This obviously facilitates elimination of the acid hydrogen atom from the complex molecule and thus promotes the reaction.



Methacrylonitrile<sup>9</sup> has no  $\alpha$ -hydrogen and therefore in the first stage of the reaction an addition product is formed.

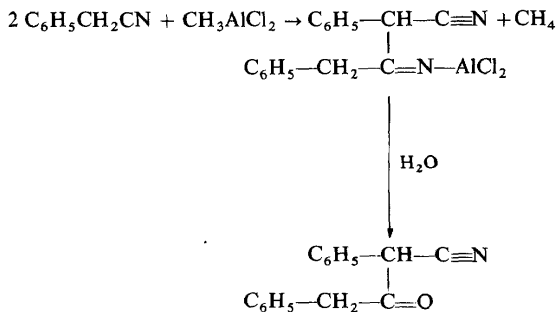


As the reaction proceeds, methane is evolved and oligomers are formed. Methane is produced as a result of elimination occurring in the addition product.

Acrylonitrile<sup>28</sup> reacts with methylaluminium compounds to yield methane and dihydro- and hexahydropyrimidine derivatives. In these reactions trimethylaluminium is the most reactive compound, and this elimination reaction appears to follow a rather involved course.

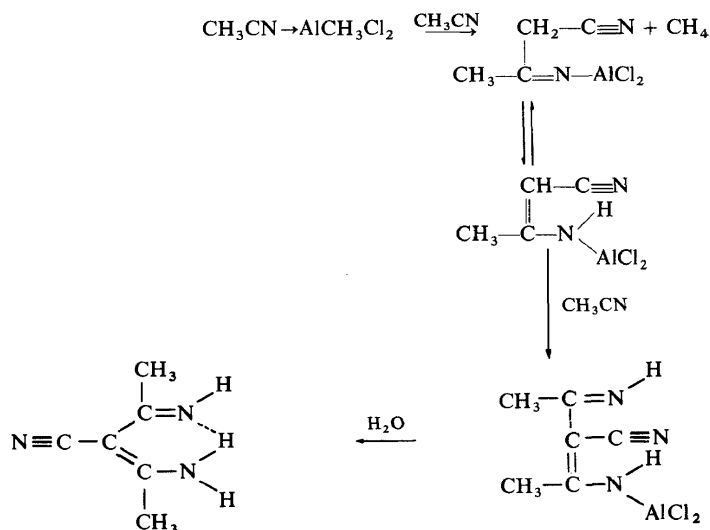
As a rule, elimination products are labile and undergo further transformations *in situ*.

Phenylacetonitrile reacts with methylaluminium dichloride<sup>24</sup>, at the mole ratio of 2:1, at an elevated temperature to yield a dimer which on hydrolysis gives a ketonitrile:

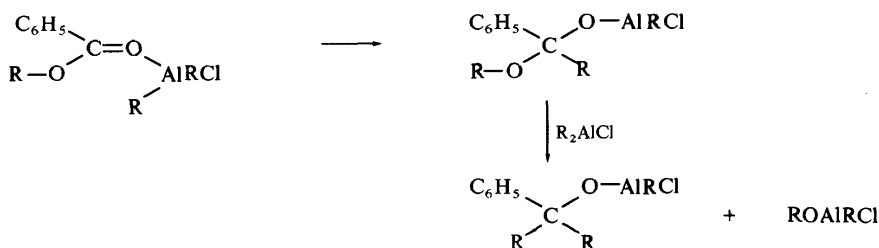


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Acetonitrile forms a trimer when treated with methylaluminium dichloride<sup>25</sup>.



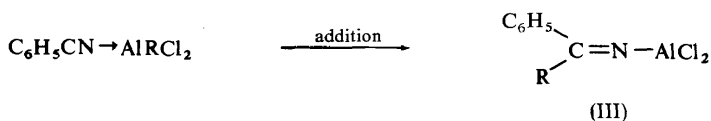
Methyl benzoate<sup>27</sup> reacts with dimethylaluminium chloride at the boiling temperature of heptane to yield methane and methyl chloride, and a tertiary alcohol as the major product of subsequent hydrolysis. The alcohol is formed as the result of addition:

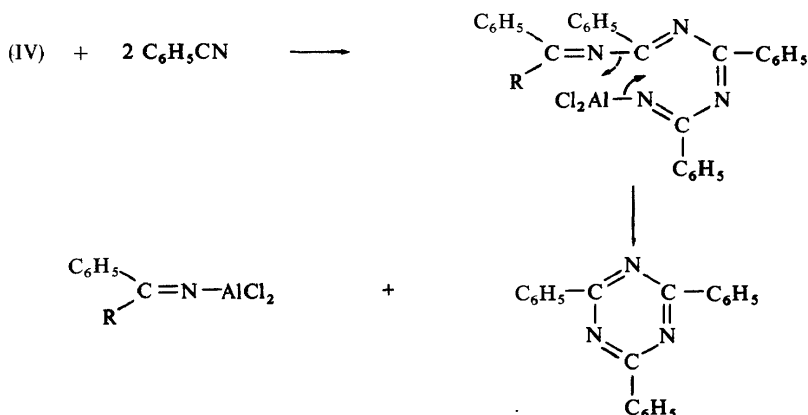
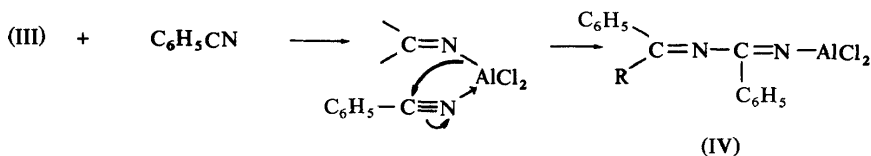


A tertiary alcohol may also be formed by a reaction between the products of addition and elimination.

The products of addition, reduction, and elimination may undergo further transformations which frequently include insertion and cyclization reactions.

The product of the addition reaction of a methylaluminium compound to benzonitrile<sup>29</sup> reacts, in appropriate conditions, with a second or with more benzonitrile molecules. These reactions involve insertion of the donor molecule to the N—Al or the C—H bonds.





The insertion reaction of the benzonitrile molecule to the N—Al bond is facilitated by an increase in the number of chlorine atoms bonded to the aluminium atom, i.e. by an increase in the electron-accepting ability of the aluminium. The ultimate product is 2,4,6-triphenylpyrimidine, formed in subsequent insertion and cyclization reactions.

From this review it is evident that the reactions of organoaluminium compounds with electron donors frequently involve several simultaneous reactions which primarily include addition, reduction, elimination, insertion, and cyclization.

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