REACTION OF TRIETHYLALUMINIUM WITH BENZONITRILE*

STANISŁAW PASYNKIEWICZ AND STANISŁAW MACIASZEK

Department of Organic Technology I, Institute of Technology (Politechnika), Warsaw (Poland)
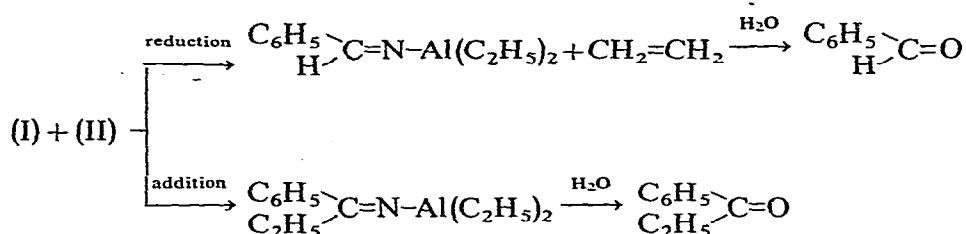
(Received July 15th, 1968)

SUMMARY

The reaction of triethylaluminium with benzonitrile has been investigated. At 150°, benzonitrile is simultaneously alkylated and reduced. The yields of the reaction products vary with the reactant mole ratio. As the triethylaluminium: benzonitrile ratio is increased, the yield of reduction product decreases and that of addition product rises. The reaction mechanism is discussed.

The reactions of methylaluminium compounds and triphenylaluminium with benzonitrile have already been investigated[1-3]. The structures of the complexes of the organoaluminium compounds with nitriles were established in terms of IR[4] and heat-of-formation studies[5].

In this investigation the reaction between triethylaluminium (I) and benzonitrile (II) was examined. It was found to proceed in two directions to yield products of reduction and addition, *viz.*,

$$(I) + (II) \begin{cases} \xrightarrow{\text{reduction}} \underset{H}{\overset{C_6H_5}{>}}C=N-Al(C_2H_5)_2 + CH_2=CH_2 \xrightarrow{H_2O} \underset{H}{\overset{C_6H_5}{>}}C=O \\ \\ \xrightarrow{\text{addition}} \underset{C_2H_5}{\overset{C_6H_5}{>}}C=N-Al(C_2H_5)_2 \xrightarrow{H_2O} \underset{C_2H_5}{\overset{C_6H_5}{>}}C=O \end{cases}$$

The results are summarized in Table 1 and presented graphically in Fig. 1. As the (I)/(II) reactant mole ratio is raised, the yield of the reduction product decreases and that of the addition product increases. The reaction time was 4 h.

When benzonitrile is used in large excess ((I)/(II) ≪ 1), the reduction is the predominant reaction; at a (I)/(II) mole ratio of 0.179, the aldehyde and the ketone yields were 43% and as low as 7%, respectively. When triethylaluminium is used in large excess ((I)/(II) ≫ 1), the addition reaction predominates; at a (I)/(II) mole ratio of 4.18, the aldehyde and the ketone yields were 5.9% and 66%, respectively. The ratio of the reduction/addition yields in relation to the reactant mole ratio are presented in Fig.2.

TABLE 1

THE ALDEHYDE AND KETONE YIELD IN
RELATION TO THE REACTANT MOLE RATIO

Molar ratio $(C_2H_5)_3Al$: C_6H_5CN	Yields aldehyde (%)	Yields ketone (%)
0.179	43.0	7.1
0.500	37.5	7.2
0.645	34.5	9.8
0.900	25.0	18.2
1.200	19.0	31.5
1.540	15.5	40.7
1.65	14.0	47.5
2.80	7.5	59.8
3.65	6.0	63.0
4.18	5.9	66.0

TABLE 2

THE TOTAL ALDEHYDE AND KETONE YIELD AT
VARIOUS REACTION TEMPERATURES

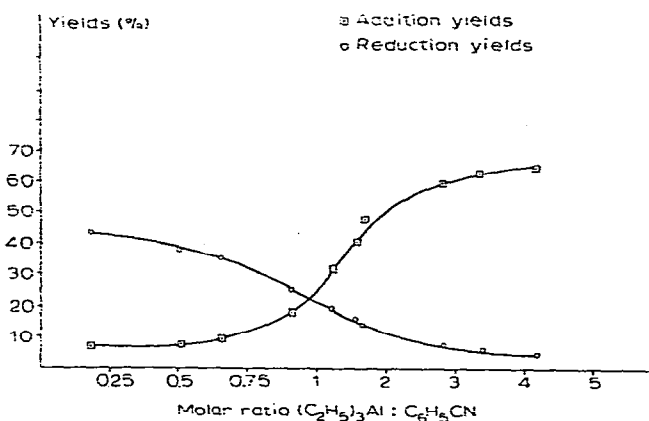| Molar ratio $(C_2H_5)_3Al$: C_6H_5CN	Temp. (°C)	Yields (%)
1.82	110	36
1.84	130	57.0
1.78	150	61.5
1.78	165	38.0

Fig. 1. Aldehyde and ketone yields as a function of the reactant molar ratio.
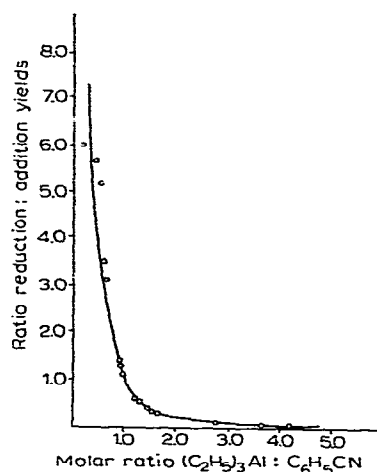Fig. 2. The ratio of the reduction/addition yields as a function of the reactant mole ratio.
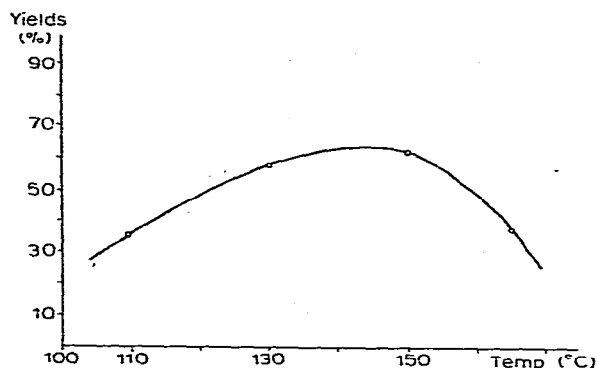

Fig. 3. The total aldehyde and ketone yield as a function of the reaction temperature.

The total yield of the overall process including both addition and reduction was examined as a function of temperature (Table 2, Fig. 3).

At a (I)/(II) mole ratio of 1.8 and a reaction time of 4 h, the highest aldehyde and ketone yields were obtained at 150°. Above and below 150°, the overall yield diminishes.

DISCUSSION

At a reactant mole ratio of 1 : 1, the reaction of triethylaluminium with benzonitrile gives the following complex:

$$\overset{(+)\ (-)}{C_6H_5-C\equiv N-Al(C_2H_5)_3}$$

sp

(III)
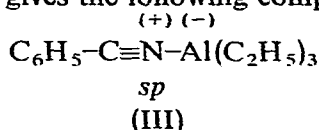
Its structure at room temperature was discussed in an earlier paper[4,5]. The complex (III) is not reactive because the nitrile carbon atom does not have a well-defined positive charge and, owing to the linear structure of the complex, is far away from the ethyl group.

At temperatures elevated by energy supplied from outside, the charge distribution and the structure of the complex may become affected.

$$\underset{sp^2}{\overset{\displaystyle C_6H_5}{\underset{(+)}{}}\underset{C=N}{}\underset{(-)}{}\underset{Al(C_2H_5)_3}{}}$$
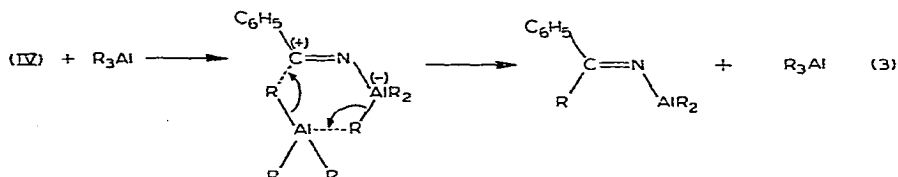
(IV)
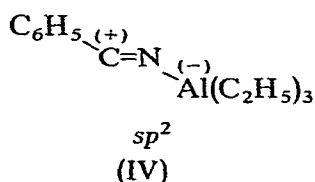
In this complex (IV) the nitrile carbon atom has acquired a positive charge and its distance from the ethyl group has become much shorter than that in the complex (III). The fundamental conditions necessary for the reactivity of complex (IV) are satisfied and it can react to give either a reduction (1) or an addition product (2).
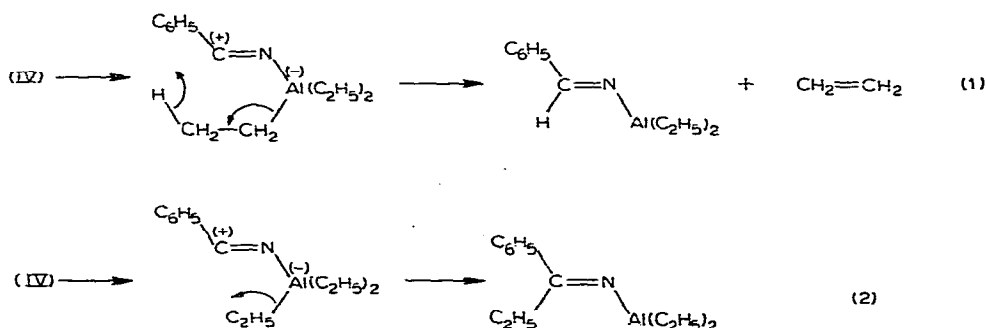
At 150° and a (I)/(II) mole ratio of 1 : 4, reduction (1) proceeds with a yield of about 40%. Under the same conditions, the yield of the addition (2) is about 7%.

These data show that at the prevailing conditions (150°, 4 h), the reduction proceeds at a much higher rate than the addition. However, this interpretation does not explain the progressive decrease of reduction yield and the gradual increase of addition yield with rising reactant mole ratio and the roles of benzonitrile and triethylaluminium in the reactions carried out with either of the two used in large excess ((I)/(II) < 1 and (I)/(II) > 1, respectively) must therefore be resolved.

In earlier investigations[1,3] the addition was found to proceed with higher yields also at lower temperatures, when the mole ratio of an organoaluminium compound to benzonitrile was greater than unity. In this case, complex (IV) reacts with the organoaluminium molecule in a favourable six-centre system, because of contraction of the distance between the ethyl group and the nitrile carbon atom, with electron transfer to give an addition product (3)

$$(IV) + R_3Al \longrightarrow \begin{array}{c} C_6H_5 \\ \diagdown \scriptstyle{(+)} \\ C = N \\ R \diagup \quad \diagdown \scriptstyle{(-)} \\ \diagup \quad \quad AlR_2 \\ Al\text{-}\text{-}R \\ \diagup \diagdown \\ R \quad R \end{array} \longrightarrow \begin{array}{c} C_6H_5 \\ \diagdown \\ C = N \\ R \diagup \quad \diagdown \\ \quad \quad AlR_2 \end{array} + R_3Al \quad (3)$$

Reaction (3) proceeds much faster than reaction (2) or (1). Reinheckel and Jahnke[6] have studied the reaction of triethylaluminium with benzonitrile at 80° and found that at reactant mole ratios of 2:1 and 1:1 the addition yield was 77% and 8%, respectively. No reduction occurred at 80°. These data are consistent with our results and confirm our conclusion concerning the rates of reactions (1), (2) and (3). This explains the increase in the yield of addition and the decrease in the yield of reduction as the proportion of triethylaluminium in the reaction mixture is raised above the equimolar ratio, i.e., (I)/(II) > 1. The rise in concentration favours the encounter of a triethylaluminium molecule with a complex (IV) molecule and the consequent addition (3). Since reaction (3) proceeds more readily than reaction (1), the former increases and the latter decreases in yield as the triethylaluminium concentration in the reaction mixture is raised.
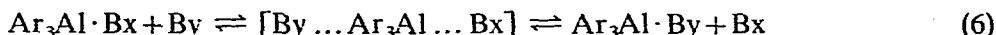
At ratios (I)/(II) < 1, the reaction mixture contains complex (III) or (IV) and free benzonitrile. If complex (IV) reacts according to eqn. (1) or (2), the yields of reduction and addition would be independent of the reactant mole ratio. However, the experimental data showed that as the benzonitrile proportion is decreased, the yield of reduction diminishes steadily and that of addition increases (Table 1, Fig. 1).

Let us consider a reacting system comprising the complex $PhCN \cdot AlR_3$ and free benzonitrile. Mole[7] has shown that, on treatment with a Lewis B base, complexes of organoaluminium compounds with ethers, amines, and benzonitrile react with replacement of their bases, and the following equilibrium becomes established:

$$Bx + Ar_3Al \cdot By \rightleftharpoons Ar_3Al \cdot Bx + By \qquad (4)$$

Equation (4) continues to hold also for $Bx = By$. In the majority of cases the equilibrium is established within a short period of time at room temperature. Mole has considered two plausible mechanisms, (5) and (6), of the base exchange:

$$Ar_3Al \cdot Bx \rightleftharpoons Ar_3Al + Bx \qquad (5a)$$

$$Ar_3Al + By \rightleftharpoons Ar_3Al \cdot By \qquad (5b)$$

$$Ar_3Al \cdot Bx + By \rightleftharpoons [By \ldots Ar_3Al \ldots Bx] \rightleftharpoons Ar_3Al \cdot By + Bx \qquad (6)$$

Mechanisms (5) and (6) are analogous to S_N1 and S_N2 mechanisms, respectively. At room temperature, mechanism (6) is more likely to occur.

In the present case, a similar replacement of base takes place (eqn. (4)), *i.e.*, the complexed benzonitrile is converted into free benzonitrile, whereby $Bx = By = ArCN$. At 150°, the replacement of base may proceed by mechanism (5). As the result of the considerable amount of energy supplied from outside, the complex (III) molecule may decompose to yield triethylaluminium and benzonitrile molecules (7).

$$ArCN \cdot Al(C_2H_5)_3 \rightleftharpoons ArCN + (C_2H_5)_3Al \qquad (7)$$
$$(III)$$
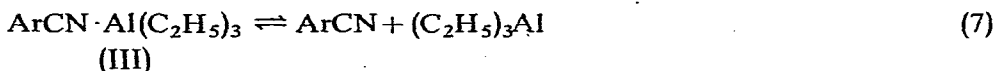
The free triethylaluminium molecule reacts immediately with the first molecule encountered. If this is a benzonitrile molecule, the starting complex (III) will be re-formed, but if it is a complex (IV) molecule, reaction (3) may follow and an addition product will be formed.

The above reaction scheme explains satisfactorily the relationship between the addition and reduction yields and the reactant mole ratio. The higher the benzonitrile concentration in the reaction medium, the more likely is the formation of complex (III) from the triethylaluminium afforded by reaction (7), and the more probable is reduction (1). On the other hand, at low benzonitrile concentrations, the reaction of the free triethylaluminium molecule with complex (IV), and thus addition (3), becomes more probable. Reaction (2) also must be taken into account, but, as demonstrated above, it proceeds much more slowly than reaction (3).

At a reactant mole ratio of 1 : 1, reaction (1) rate increases as the temperature is raised. At 80°, reduction is not noticeable[6], but at 150° it proceeds with 20% yield, and at still higher temperatures (190–200°) it becomes the predominant reaction[8].

Wade *et al.*[8–10] established the structure of the final products of reduction (1) and addition (2): $ArCH : NAl(C_2H_5)_2$ and $Ar(C_2H_5)C : NAl(C_2H_5)_2$. When isolated in the pure state these compounds occur in the form of dimers (V):

R\   /R
    Al
   /   \
 >C=N   N=C<,
   \   /
    Al
  R/   \R
    (V)
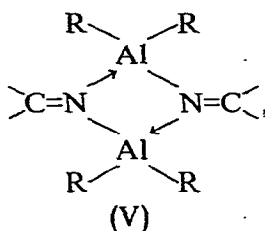
The structure of complexes which may be formed with benzonitrile or with an organoaluminium compound used in excess have not yet been reported.

EXPERIMENTAL

1. *Reactants*

Triethylaluminium was prepared by the method described earlier[11,12]. Benzonitrile (Xenon, Łódź, Poland) was dried over anhydrous magnesium sulphate, distilled twice in a nitrogen atmosphere and stored over type 4A molecular sieves.

2. Method

Reactions were carried out in an atmosphere of dried deoxygenated nitrogen. A measured amount of triethylaluminium was placed in a round-bottomed double-necked flask (25 ml) equipped with an efficient reflux condenser connected to a brine bottle. The bottle was used to collect the gases evolving during the reactions. The bottom outlet from the bottle was connected through a controlled hydraulic seal to a measuring cylinder in which the brine displaced by the gases from the bottle was collected and measured. The flask was cooled to $-60°$ and an appropriate amount of benzonitrile was introduced by means of a hypodermic syringe. After the benzonitrile had been added dropwise, the flask was maintained for 15 min at room temperature and then placed in a heated thermostat. The reaction was continued for 4 h at a constant temperature ($\pm 0.1°$). The flask was then cooled to $0°$ and the products slowly hydrolyzed with a 5% sodium hydroxide solution in ethanol–water (80:20). The hydrolyzate was transferred to a measuring flask (250 ml) and made up to the mark with the solution used for hydrolysis. The aldehyde and ketone formed were determined together by the gravimetric method using 2,4-dinitrophenylhydrazone. Aldehyde was determined indirectly by measuring the volume of ethylene contained in the reaction gases. The ketone yield was calculated as:

$$\text{ketone } (\%) = \frac{1000\,(N/n)m - 286x}{314}$$

where m is the hydrazone weight,
　　　　n is the weight of reactant (I) or (II) used in an insufficient amount,
　　　　N is molecular weight of this reactant,
　　　　x is aldehyde yield (%),
　　　286 is molecular weight of aldehyde hydrazone,
　　　314 is molecular weight of ketone hydrazone.

REFERENCES

1　S. Pasynkiewicz, W. Kuran and E. Soszyńska, *Roczniki Chem.*, 38 (1964) 1285.
2　S. Pasynkiewicz and W. Kuran, *Roczniki Chem.*, 39 (1965) 979.
3　S. Pasynkiewicz and W. Kuran, *Roczniki Chem.*, 39 (1965) 1199.
4　K. Starowieyski and S. Pasynkiewicz, *Roczniki Chem.*, 40 (1966) 47.
5　K. Starowieyski, S. Pasynkiewicz and M. Bolesławski, *J. Organometal. Chem.*, 10 (1967) 393.
6　H. Reinheckel and D. Jahnke, *Ber.*, 97 (1964) 2661.
7　T. Mole, *Australian J. Chem.*, 16 (1963) 801.
8　J. E. Lloyd and K. Wade, *J. Chem. Soc.*, (1965) 2662.
9　J. R. Jennings, J. E. Lloyd and K. Wade, *J. Chem. Soc.*, (1965) 5082.
10　K. Wade and B. K. Wyatt, *J. Chem. Soc.*, (1967) 1339.
11　S. Pasynkiewicz, W. Dahlig and K. Starowieyski, *Roczniki Chem.*, 36 (1962) 1582.
12　S. Pasynkiewicz and W. Dahlig, *Przemysł Chem.*, 39 (1960) 300.