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REACTION OF TRIETHYLALUMINIUM WITH ESTERS

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The purpose of this work is to examine the effect of substituents on the yield of carbonyl compounds in reactions of triethylaluminium with esters.

Our earlier investigations on the reactions of organoaluminium compounds with nitriles[1-3] and ketones [4,5] have shown the yield of addition and reduction to depend upon the extent of the partial positive charge on the carbonyl or nitryl carbon atom. No systematic investigations on this problem have so far been conducted. A change of the substituent in an aromatic ester affects the distribution of electric charges in the molecule. It also changes the extent of the partial positive charge on the carbonyl carbon atom. Knowledge of yield of reaction products enables us to estimate the influence of the extent of this charge on the reaction course.

So far, reactions of organoaluminium compounds with esters have been very little investigated. Reactions of diisobutylaluminium hydride and triisobutylaluminium with esters have been studied by Ziegler *et al.*[6]. It was found that esters are reduced to corresponding alcohols in high yields. Zakharkin and Khorlina[7] have investigated the reaction of diisobutylaluminium hydride with esters and obtained aldehydes. The reaction proceeded at room temperature with good yields. Also, Zakharkin and Khorlina[8] have examined the reaction of sodium aluminium diisobutyl dihydride, $NaAl(iso\text{-}C_4H_9)_2H_2$, with esters and at $-70°$ obtained aldehydes. Reinheckel[9] has studied the reactions of higher aliphatic esters with dialkyl aluminium hydrides and obtained alcohols.

Organoaluminium compounds such as alkyl aluminium hydrides, triisobutylaluminium and complexes of the type $NaAl(iso\text{-}C_4H_9)_2H_2$, are strong reductive reagents. Therefore, their reactions with esters can afford only the products of reduction, *viz.*, aldehydes and alcohols. So far, reactions of esters with trimethylaluminium and alkyl aluminium chlorides have not been described.

RESULTS

The present paper deals with reactions between triethylaluminium and esters of the type $p\text{-}XC_6H_4COOC_2H_5$ where $X = OCH_3, CH_3, H, Cl$, and CN. The reactions were carried out in a thermostated glass vessel in nitrogen atmosphere. The mixture was hydrolyzed with aqueous 20% sodium hydroxide and the organic material was extracted with ether. Then the ether was distilled off and the carbonyl compounds present in the reaction mixture were determined gravimetrically.

Triethylaluminium was found to react with esters at 150° in two directions to yield products of reduction and addition:

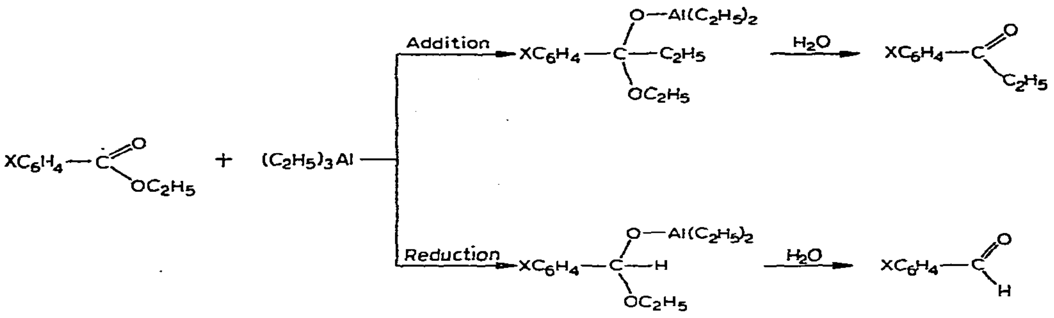


TABLE 1

YIELD OF ADDITION AND REDUCTION PRODUCTS IN THE REACTION OF TRIETHYLALUMINIUM WITH *p*-SUBSTITUTED ETHYL BENZOATES[a]

X	*Yield (%) after:*		
	6 *h*	6 *h*[b]	4 *h*
OCH_3	17	15	5
CH_3	18	16	6
H	20	18	8
Cl	22	19	11
CN	30	24	20

[a] Et_3Al/ester = 1/1; temperature 150°. [b] In xylene as solvent.

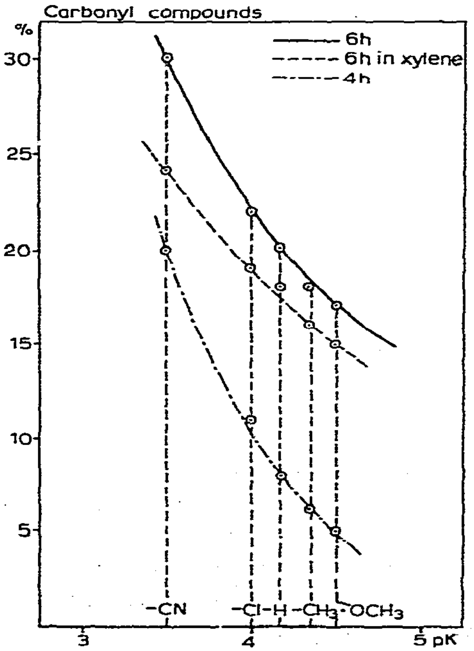


Fig. 1. Yield of carbonyl products *vs.* strength of the ester's parent acid. Temperature 150°, time 6 h (———), 6 h (– – – –) in xylene, and 4 h (–·–·–).

Table 1 gives the yields of carbonyl compounds (aldehydes and ketones) obtained in the reaction of triethylaluminium with esters in relation to the substituent used. In each case, the yields are seen to increase in the following order: $OCH_3 < CH_3 < H < Cl < CN$. The time of reaction had a great influence on the yield. With the time protracted from 4 to 6 h, the yield doubled. The type of solvent had a much smaller effect, but its presence decreased the yield. The yield of the products of reduction and addition reactions was plotted in relation to the strength (p*K*) of the ester's parent acid (Fig. 1). It is evident from Fig. 1 that the yield of carbonyl compounds is related to the strength of the parent acid and rises as the strength of the acid is increased.

DISCUSSION

The present investigations indicate that esters are compounds of low reactivity. The reactions (at 150°) of triethylaluminium with various esters range from 5 to 30% in the yield of carbonyl compounds, *i.e.* the products of addition and reduction. Esters are much less reactive than ketones. Diethyl ketone reacted with triethylaluminium to yield 82% of carbonyl compounds at 25°. Even the slightly reactive diisobutyl ketone reacted easily with triethylaluminium to yield a reduction product in a considerable amount. Also, esters are less reactive than nitriles. For example, benzonitrile reacted with triethylaluminium to give 45% of carbonyl compounds, whereas ethyl benzoate in the same conditions yielded only 8% of corresponding carbonyl compounds (Table 2).

TABLE 2

YIELD OF CARBONYL COMPOUNDS IN THE REACTION OF TRIETHYLALUMINIUM WITH ORGANIC COMPOUNDS[a]

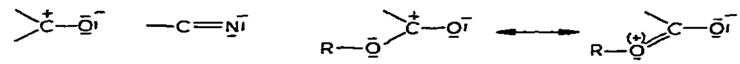
Organic compound	*Temp.* (°C)	*Time* (*h*)	*Yield* (%)	*Ref.*
Et_2CO	25	3	82	4
iso-Bu_2CO	65	3	86	4
iso-Bu_2CO	80	3	92	4
C_6H_5CN	150	4	45	10
C_6H_5COOEt	150	4	8	
C_6H_5COOEt	150	6	20	

[a] Et_3Al/organic compound = 1/1.

How may we explain the considerable differences in the reactivity of esters compared with ketones and nitriles. It is clear from our previous investigations that the reactivity of compounds possessing either a carbonyl or a nitryl group depends for a given organoaluminium compound primarily upon the following factors:

(*a*) the extent of the partial positive charge on the carbonyl or nitryl carbon atom,
(*b*) the geometric structure of a complex, and
(*c*) steric hindrance.

The following formulae of ketone, nitrile and ester molecules show the most positively charged carbon atom to occur in ketones.

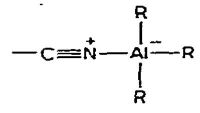


The charge of the nitrile carbon atom is smaller owing to partial compensation by the carbon–nitrogen double bond. Similarly, the positive charge of the ester carbon atom is considerably reduced as a result of shift of electrons from the OR group to the carbonyl carbon atom.

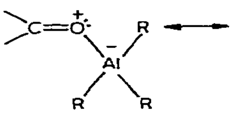
The molecular polarization, and thus the positive charge on the carbonyl carbon atom, increases when the given organic and organoaluminium compounds form a complex.

It is known from our earlier works that the first step of this reaction involves formation of a donor–acceptor complex between either the oxygen or nitrogen and aluminium atom. The geometric structure of such a complex highly affects its reactivity. We have shown[11] the complexes of nitriles with organoaluminium compounds (at room temperature) to possess structure (I) (∢ CNAl = 180°). In the complex (I), the distance between the R radical and the nitrile carbon atom is fairly large; this presumably renders intramolecular rearrangement unfeasible.

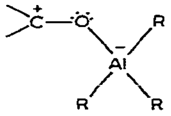
The geometric structure of ketone/organoaluminium complexes may be illustrated by the formulae (IIa) and (IIb). In each of them, the angle ∢ COAl ⩽ 120°, and thus the R–C distance is much smaller than that in the structure (I). Therefore, intramolecular rearrangement proceeds easier and ketones are more reactive than nitriles.



(I)



(IIa)



(IIb)

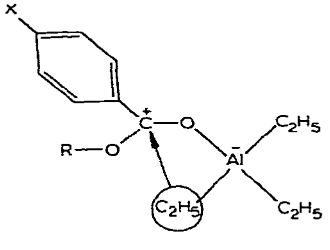
Complexes of esters with organoaluminium compounds have the geometric structure similar to that of ketone complexes[12]. With esters, however, the geometric structure of the complex is too unfavourable to permit an intramolecular rearrangement. The complex is only slightly reactive, because of its small positive charge on the carbonyl carbon atom and steric hindrance. In the case of ethyl benzoate derivatives, the presence of bulky (phenyl and ethoxy) groups surrounding the carbonyl carbon atom considerably impedes intramolecular rearrangement of the ethyl group and its pair of electrons.

Steric hindrance has been shown to have considerable influence on the reactions of ketones with organoaluminium compounds[4]. At 40°, diisopropyl ketone failed to react with triethylaluminium, whereas diethyl ketone (small steric hindrance) reacted in 100% at 0°.

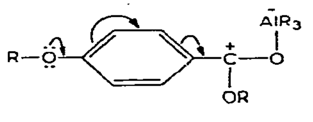
All this argumentation indicates that, if an organic compound reacts with an organoaluminium compound according to the mechanism of electron shift in multicentered transition states, its reactivity depends upon the electron-acceptor property of the carbon atom which accepts electrons, upon the geometric structure of the reacting complex and steric hindrance. However, these factors are not of equal consequence and they are related to the nature of the reacting organic compound.

The results presented in Table 1 and in Fig. 1 show that the extent of the positive charge on the carbonyl carbon atom has a great influence on the yield of the reactions between triethylaluminium and esters.

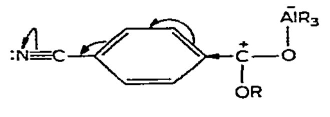
The reactive complex of an ethyl benzoate derivative and triethylaluminium may be presented by (III). For various X substituents, the geometric structure and steric hindrance of the complex are constant and the only variable is the electrophilicity of the carbonyl carbon atom. Electron-donating substituents reduce the positive charge on the carbon atom (IV) and thus render rearrangement difficult. Electron-accepting substituents have the opposite effect (V). The reaction yields differ very much and for the terminal substituents, OCH_3 and CN, change 2–4-fold.



(III)



(IV)



(V)

The effect of the carbonyl carbon electrophilicity on the reaction yield is presented in Fig. 1. The yield of the reaction rises systematically as the strength of the parent acid of the ester used is increased. Of course, it is the substituent X which determines the acid strength.

EXPERIMENTAL

Materials

Triethylaluminium (99.6%) was prepared as previously described[13]. Commercial ethyl benzoate, b.p. 212–213°, was used. Ethyl *p*-methylbenzoate, b.p. 227–228°, was obtained by reaction of *p*-methylbenzoyl chloride with ethyl alcohol. Ethyl *p*-methoxybenzoate, b.p. 139–141°/14 mm, was prepared from anisic acid and ethyl alcohol. Ethyl *p*-chlorobenzoate, b.p. 236–238°, was obtained from *p*-chlorobenzoic acid and ethyl alcohol. Ethyl *p*-cyanobenzoate, m.p. 53–54°, was prepared from *p*-cyanobenzoic acid and sodium ethoxide. Each ester was dried over anhydrous magnesium sulphate and fractionated before the reaction.

Technique

Each reaction was carried out in nitrogen atmosphere. Triethylaluminium, 1.5 ml, was injected by means of a syringe into a round-bottomed flask (10 ml). The flask was connected to an empty rubber balloon and cooled to −60° and an ester, 1 mole per 1.1 mole of triethylaluminium, was added. The flask was kept 15 min at room temperature, then placed in an ultrathermostat and heated for 6 or 4 h at 150°. The reaction mixture was hydrolyzed with aqueous 20% sodium hydroxide (40 ml) and allowed to stand 0.5 h at room temperature until no aluminium hydroxide remained undissolved. The organic layer was extracted with ether (3 × 15 ml). The combined organic layers were washed with 10% hydrochloric acid (2 ml) and water and dried for 24 h over anhydrous magnesium sulphate (4 g). The ether was distilled off at room temperature and reduced pressure (35–40 mm). An aliquot for analysis, 0.3–0.5 g, was placed in a preweighed ampoule. Carbonyl compounds were determined with 2,4-dinitrophenylhydrazone. The mean of the aldehyde and ketone molecular weights was used for calculations. The error of the gravimetric analysis is related to the aldehyde-to-ketone ratio of molecular weights and is fairly small. For example, the highest absolute error for the 6-h reaction of ethyl *p*-cyanobenzoate was equal to ±1.6% referred to pure aldehyde or ketone as product instead of a mixture thereof. The amount of the aldehyde obtained in the reaction between ethyl benzoate and triethylaluminium was determined in terms of the ethylene formed.

SUMMARY

Reactions of triethylaluminium with certain esters were investigated. The reactions were found to afford products of addition and reduction. The effect of the carbonyl carbon electrophilicity on the reaction yield was investigated. The reaction mechanism is discussed.

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