

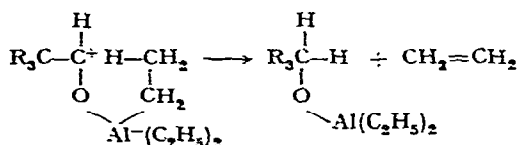
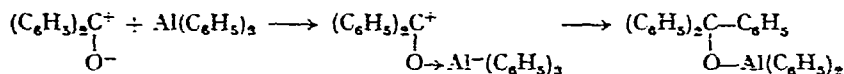
## THE REACTION OF ORGANOALUMINIUM COMPOUNDS WITH KETONES

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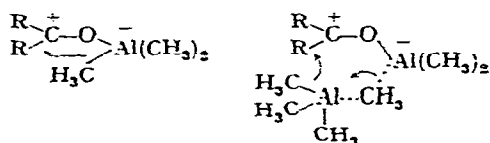
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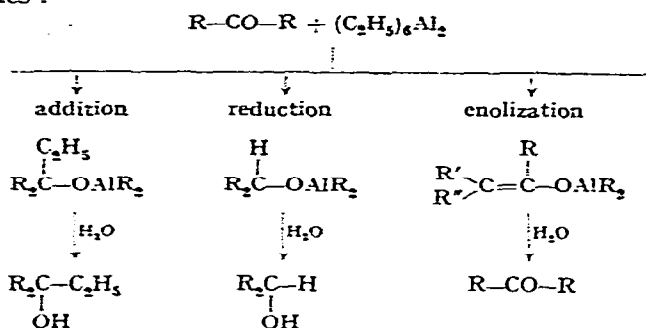
Like Grignard reagents organoaluminium compounds can react with ketones to give products of addition, reduction and enolization reactions. Gilman and Marple<sup>1</sup> investigated the reaction of triphenylaluminium etherate with benzophenone and obtained triphenylcarbinol as the result of the addition reaction. Reactions of triethylaluminium etherate with certain chloroketones were investigated by Meerwein<sup>2</sup> and his co-workers, and resulted in the formation of corresponding secondary carbinols, as reduction products. The reduction reaction of ketones with diisobutylaluminium hydride and triisobutylaluminium was studied more thoroughly by Ziegler<sup>3</sup> and his co-workers. It was found, that in the case of cyclohexanone and acetophenone, enolization as well as reduction products were formed. As a result of the experiments carried out by Gilman<sup>1</sup> and Meerwein<sup>2</sup>, the following mechanism for the addition and reduction reactions was proposed by Wittig and Bub<sup>4</sup>.



In our previous paper<sup>5</sup> the reactions of propiophenone with trimethylaluminium were investigated and methylethylphenylcarbinol was found as the sole reaction product. The yield of reaction product depends upon the molar ratio of the reagents ketone/trimethylaluminium and reaches 100% when the molar ratio is equal to 1:2. From experimental data it was proposed that rearrangement of the reaction complex, for the reagent-ratio 1:1, goes via a four-centered transition state, and for the reagent ratio 1:2 via six-centered transition state.



Hitherto, it has been found that the addition reaction takes place only with those organoaluminium compounds (triphenylaluminium<sup>1</sup> and methylaluminium compounds<sup>2</sup>) where the reduction reaction is impossible. Therefore, it seemed reasonable to investigate the reaction of ketones with ethylaluminium compounds. These compounds can undergo the addition as well as the reduction reaction. Our aim was to examine the ratio of the addition to reduction reaction product yields as function of the ratio of the reagents used. It was also possible, in this way, to confirm the mechanism of the reaction of organoaluminium compounds with nitriles<sup>6,7</sup> and ketones<sup>5</sup>.



## RESULTS

In the present paper the results of the reaction between diethyl ketone, diisopropyl ketone and ethylaluminium compounds are described. The reactions were carried out in glass apparatus filled with nitrogen, the reaction vessel was heated with the aid of ultrathermostat. After hydrolysis with 20% aqueous potassium hydroxide the organic material was extracted with ether. The ether extracts were dried, filtered, and analyzed by gas-liquid chromatography.

The results of the reaction of diethyl ketone with triethylaluminium at constant temperature are presented in Table I and Fig. 1. As can be seen from the given data, the yield of addition reaction product increases, and the yield of reduction product decreases, with increasing reagent-ratio triethylaluminium/ketone. The yield of

TABLE I

PRODUCT DISTRIBUTION AND RATIO OF ADDITION TO REDUCTION PRODUCTS IN THE REACTION BETWEEN TRIETHYLALUMINIUM AND DIETHYL KETONE

Ratio of (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> -Al to ketone	Yield, %			Ratio of addition to reduction
	Addition	Reduction	Enolization	
0.25	40.0	37.2	22.8	1.08
0.5	46.0	31.0	23.0	1.48
0.675	48.3	27.0	24.7	1.8
1.0	56.0	26.0	19.0	2.15
1.5	62.0	19.0	18.0	3.26
2.0	65.5	15.5	19.0	4.3
4.0	77.5	7.0	15.5	11.1

Reaction time 3 h; temperature 25°.

enolization reaction product depends upon the reagent-ratio only to a small extent. The results, concerning dependence of addition, reduction, and enolization reaction product yields upon the temperature, are summarized in Table 2 and Fig. 2. Increase

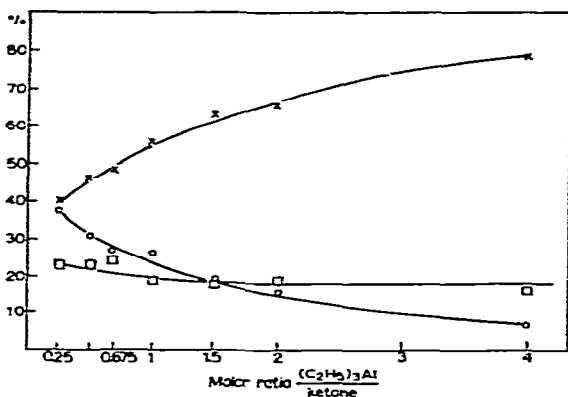


Fig. 1. The ratio of addition ( $\times$ ), reduction ( $O$ ), and enolization ( $\square$ ) yields as a function of the reagent-ratio used in the reaction of triethylaluminium with diethyl ketone. Temperature  $25^\circ$ .

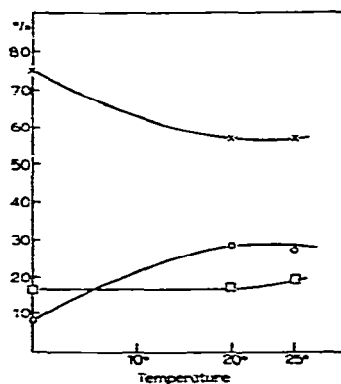


Fig. 2. Dependence of yields of addition ( $\times$ ), reduction ( $O$ ), and enolization ( $\square$ ) products on the reaction temperature. Reagent-ratio  $(C_2H_5)_3Al$ /diethyl ketone = 1.

in temperature causes a decrease in the addition reaction product yield and a higher reduction reaction product yield and has very little effect on enolization.

The results of the reaction of diisopropyl ketone with triethylaluminium, diethylaluminium chloride and ethylaluminium dichloride are summarized in Table 3. According to the data, diisopropyl ketone is much less reactive than diethyl ketone. At temperatures below  $40^\circ$  none of these three reactions occurred. In the temperature range,  $65$ – $100^\circ$ , with any reagent-ratio the addition reaction did not take place at all,

TABLE 2

YIELDS OF ADDITION, REDUCTION AND ENOLIZATION PRODUCTS AND RATIO OF ADDITION TO REDUCTION IN THE REACTION OF TRIETHYLALUMINIUM WITH DIETHYL KETONE

Temperature of reaction	Yield, %			Ratio of addition to reduction
	Addition	Reduction	Enolization	
$0^\circ$	74.0	9.5	16.5	7.8
$19^\circ$	56.1	27.5	16.4	2.0
$25^\circ$	56.0	26.0	19.0	2.15

Ratio of  $(C_2H_5)_3Al$  to ketone 1; time of reaction 3 h.

and the enolization reaction occurred to a very small extent (if any). The main reaction is reduction of the ketone. The highest reduction reaction yield was obtained when triethylaluminium was used. Diethylaluminium chloride is much less reactive and ethylaluminium dichloride did not react with diisopropyl ketone at all.

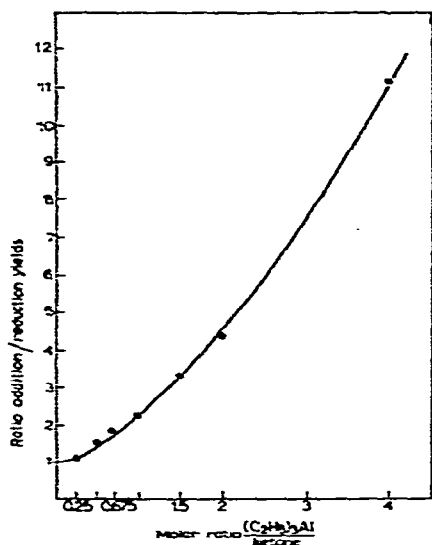


Fig. 3. The relationship between the ratio of addition to reduction product yields and molar ratio of  $(C_2H_5)_2Al$  to diethyl ketone. Temperature  $25^\circ$ .

TABLE 3

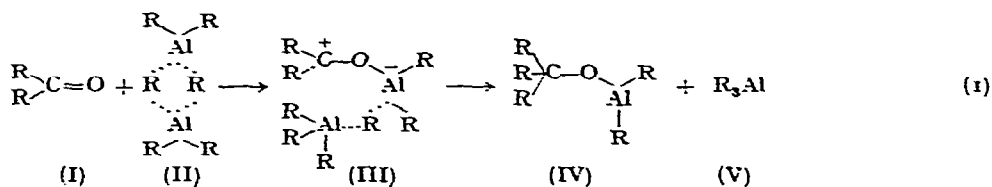
THE REACTIONS OF ALUMINIUM ETHYLS WITH DIISOPROPYL KETONE

Organoaluminium compound	Ratio of organoaluminium compound to ketone	Reaction temp., $^\circ C$	Product composition, %	
			Diisopropylcarbinol	Ketone
$(C_2H_5)_3Al$	0.5	80	49.2	50.8
$(C_2H_5)_3Al$	1.0	80	92.4	7.6
$(C_2H_5)_3Al$	2.0	80	99.1	0.9
$(C_2H_5)_3Al$	4.0	80	99.3	0.7
$(C_2H_5)_3Al$	1.0	100	80.9	19.1
$(C_2H_5)_2Al$	2.0	100	98.4	1.6
$(C_2H_5)_2AlCl$	1.0	80	91.6	8.4
$C_2H_5AlCl_2$	1.0	80	—	100
$(C_2H_5)_3Al$	1.0	65	86.3	13.7
$(C_2H_5)_2AlCl$	1.0	65	37.1	62.9
$(C_2H_5)_3Al$	1.0	40	—	100

Reaction time 3 h.

DISCUSSION

Amongst these three competitive reactions, the highest yield of addition products occurs at  $0^\circ$ , which indicates that addition reaction is fastest. Since triethylaluminium exists as a dimer at temperatures below its boiling point, the addition reaction mechanism involves, most probably, electron transfer in a six-centered transition state.

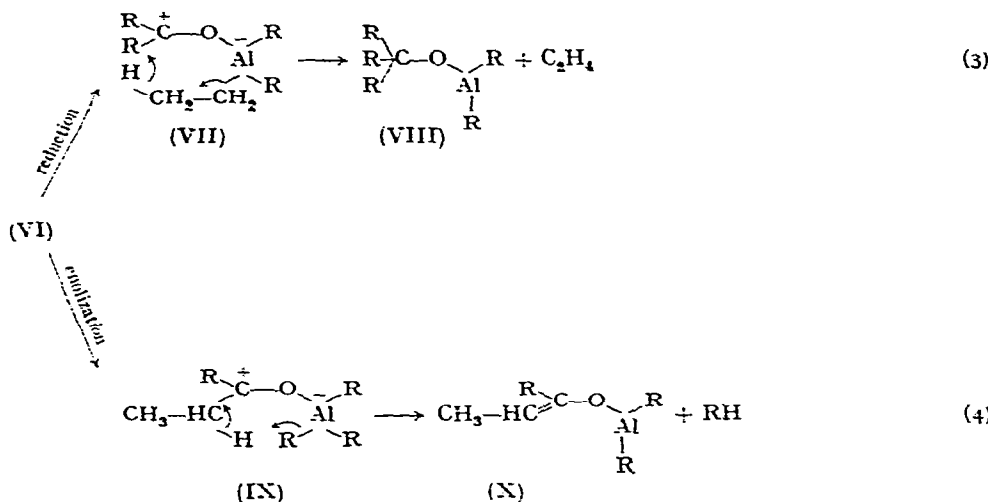


The geometric structure of this transition state (III) permits closest approach of an ethyl group to the positively charged carbon atom and this facilitates the reaction.

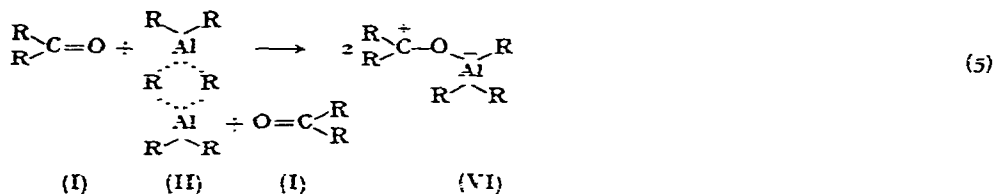
When the ketone is used in excess, a molecule of triethylaluminium (V) is formed as a result of reaction (1). This molecule (V) may react with a molecule of ketone to form a complex (VI).



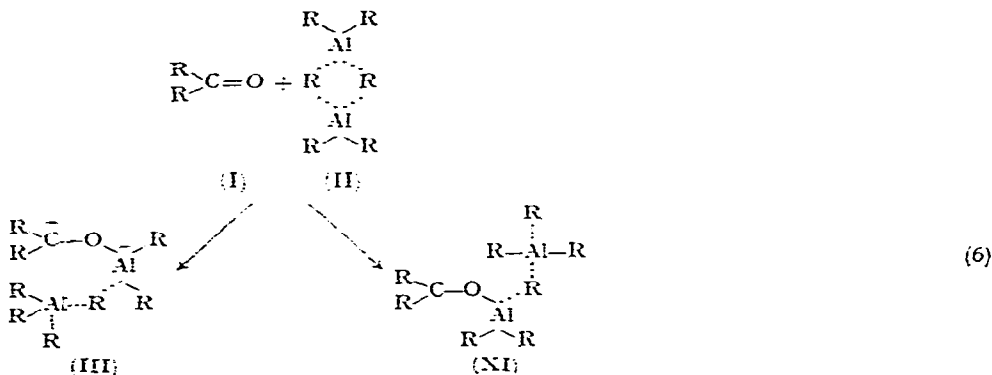
Because of its geometric structure (with a large distance between the ethyl group and the positively charged carbon atom), the complex (VI) does not react to give the addition reaction product but reduction (eqn. 3) and enolization (eqn. 4) occur instead.



If the reaction proceeded according to the eqns. (1-4), the addition product should attain 50% of the total yield. Reduction and enolization reaction product yields should constitute the remainder. When the reaction is carried out in the presence of a large excess of ketone (2- and 4-fold), the yield of addition reaction product is less than 50%. This fact can be explained by the simultaneous attack of two molecules of the ketone on one molecule of triethylaluminium dimer. In this case complex (VI) is formed which does not undergo the addition reaction, but only reduction and enolization.



When a greater reagent-ratio triethylaluminium/ketone is used, the probability of reaction presented by eqn. (2) is less. This leads to an increase in the addition reaction and thus to a decrease in the reduction and enolization reactions. When the reagent-ratio reaches the value 2 or more, that is one molecule of ketone reacts in the presence of one or more molecules of triethylaluminium dimer, a monomeric triethylaluminium molecule has a very small chance of collision with a free molecule of ketone and therefore the probability that reaction (2) will occur is very small. Nevertheless, even with a very large excess of triethylaluminium, reduction and enolization reactions do take place. This fact can be explained in the following way. A molecule of ketone which reacts with a molecule of triethylaluminium dimer forms a complex, in which, because of  $sp^3$  hybridisation of aluminium atomic orbitals, angles  $\angle \text{OAlC}$  and  $\angle \text{CAlC}$  should have values close to tetrahedral. Considering also the free rotation of O-Al and Al-C, one can assume, that the complex can have one of two forms, which render further reaction possible.



Complex (III), according to eqn. (1), after rearrangement gives addition product and (XI), like (VI), results in reduction and enolization.

Diisopropyl ketone reacts with triethylaluminium with much more difficulty than does diethyl ketone. The reaction yield above 65° is high and does not depend upon the reagent-ratio. Tertiary carbinol was not found in the reaction products and this indicates that an addition reaction did not occur. The high yield of reduction product indicates also that enolization occurs only to a very small extent. The course of the reduction reaction, and the complete lack of addition, and small reactivity of diisopropyl ketone can be explained by its structure. Diisopropyl ketone possesses two bulky isopropyl groups and therefore probably steric hindrance prevents the formation of a six-centered transition state (III) with the molecule of triethylaluminium dimer and the addition reaction does not take place.

The above experiments confirm the proposition of a rearrangement mechanism via a six-centered transition state with electron transfer. If the addition reaction mechanism involved the decomposition of the complex into free ions, approach of the anion  $C_2H_5^-$  to the positively charged carbon atom of the carbonyl group would not be rendered difficult by the steric requirements of the ketone. In the reduction reaction, steric hindrance is not so important because the approach of a small hydrogen atom to the carbon of a carbonyl group is much easier than the approach of an ethyl group. This renders the reduction reaction possible according to eqn. (3). The fact that a low enolization reaction yield occurs is not clear. Perhaps, under the reaction conditions, reduction is faster than enolization. This problem requires further investigation.

The lower reactivity of diethylaluminium chloride as compared with triethylaluminium, and lack of reaction with ethylaluminium dichloride agree well with reactivity data on organoaluminium compounds established previously<sup>5,6,7</sup>.

The reactivity of organoaluminium compounds, as previously observed<sup>8-11</sup> for reactions proceeding via an ionic mechanism is the reverse of that found in this work. This fact is further evidence for the reaction mechanism proposed.

## EXPERIMENTAL

### Materials

Triethylaluminium, diethylaluminium chloride, and ethylaluminium dichloride were prepared according to the method previously described<sup>12</sup>. Commercial diethyl ketone, b.p. 108°,  $n_D^{20}$  1.3122, was used. A sample of 3-pentanol, b.p. 116°,  $n_D^{20}$  1.4075, was obtained from the reaction of ethylmagnesium bromide with propionaldehyde. Triethylcarbinol, b.p. 118°,  $n_D^{20}$  1.4265, was prepared from diethyl ketone and ethylmagnesium bromide.

Diisopropylcarbinol, b.p. 132-133°,  $n_D^{20}$  1.4225, was prepared from isobutylaldehyde and isopropylmagnesium bromide. Diisopropyl ketone, b.p. 123-124°,  $n_D^{20}$  1.4001, was obtained by the oxidation of diisopropylcarbinol with chromic mixture. Ethyldiisopropylcarbinol, b.p. 117°/125 mm,  $n_D^{20}$  1.4440, was prepared from diisopropyl ketone and ethylmagnesium bromide.

### General procedure

All reactions were carried out in an atmosphere of nitrogen. A definite amount of the organoaluminium compound was introduced into a round-bottomed flask (50 ml) with the aid of a syringe. The flask, after connecting to an empty rubber balloon, was cooled to -60° and the corresponding amount of ketone was added. Subsequently the flask was left, either in room temperature for 15 min or, depending upon the temperature required, placed directly in a thermostat. The flask was heated for 3 h at constant temperature ( $\pm 0.1^\circ$ ), cooled to -60°, and the contents hydrolyzed with an aqueous 20% sodium hydroxide solution (40 ml). After the hydrolysis, the flask was allowed to stand in room temperature for 1/2 h in order to permit the remainder of the aluminium hydroxide to dissolve. The organic layer was separated and the water layer was extracted twice with ether (5 and 2 ml). The combined organic layers were washed with water and dried over anhydrous sodium sulphate (4 g) during 24 h. The ether solution was analyzed by gas chromatography using a column which had been calibrated with known mixtures of products and standards.

## SUMMARY

Reactions of ethylaluminium compounds with diethyl ketone and diisopropyl ketone were investigated. It was found that triethylaluminium reacts with diethyl ketone to give products of addition, reduction and enolization reactions. The yield of addition reaction product increases and the yield of reduction reaction product decreases when larger ratios of triethylaluminium to ketone are used, or when the temperature is lowered. Triethylaluminium and diethylaluminium chloride react with diisopropyl ketone to give reduction reaction products only. Ethylaluminium dichloride does not react with diisopropyl ketone up to 100°. The reaction mechanism is discussed.

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