NOTES

Reaction of Triethylaluminum with Ketone

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It has been found that the reaction of alkylaluminum compounds with ketones involves normal addition, reduction and enolization reactions.[1-4)]

Pasynkiewicz and Sliwa[5)] have carried out studies of the reaction of triethylaluminum with diethyl ketone and diisopropyl ketone. As a result of these experiments, they concluded that the normal addition and reduction are affected by the mole ratio of ketone/$AlEt_3$ and by the reaction temperature, while the enolization reaction is not subject to such influences.

In the course of an investigation of the reactions of methyl ketones with triethylaluminum, the present author has been interested in the fact that , although the reactions of triethylaluminum and its diethyl ether adduct with ketones yield three kinds of products resulting from addition, reduction and enolization-condensation reactions, a considerable quantity of ethane has been obtained as a further product. The amount of this gaseous product was much greater than was to be expected from the amount of the enolization-condensation product.

The present investigation was undertaken to reveal the source of these gaseous products and the mechanism of the formation of the enolization-condensation product in the reaction of ketones with triethylaluminum and its diethyl ether adduct.

Experimental

All the melting points uncorrected.

Materials. Commercial acetone (bp 55°C), methylethyl ketone (bp 78°C), methyl *n*-propylketone (bp 101°C), methyl isopropyl ketone (bp 94°C), methyl *s*-butyl ketone (bp 116°C), methyl *t*-butyl ketone (bp 105°C) methyl *n*-amyl ketone (bp 148°C), methyl isoamyl ketone (bp 142°C), and acetophenone (bp 201°C) were purified by distillation. Triethylaluminum purchased from the Ethyl Corp. was used without further purification.

Solvent. Petroleum ether was distilled, and a fraction with a bp of 35—45°C was dried over metallic sodium.

Analytical Procedure. The amounts of recovered ketone and secondary alcohol were determined by the Iddles[6)] and Verbeck[7)] methods respectively. The tertiary alcohol content was calculated from the total amount of alcohol itself determined by the active hydrogen analysis, and from the secondary alcohol content. The amounts of the gaseous products were measured, and then their components were analyzed by gas chromatography using a Okura Gas Chromatograph, Model-4000 (dimethyl sulfolane 5 m; 20°C; hydrogen gas as carrier gas). The active hydrogen content of the condensation products was determined by the Niederl[8)] method, based on the reaction with methylmagnesium iodide.

General Procedure. All the reactions were carried out in an atmosphere of dry nitrogen. A thirty-weight-percent solution of triethylaluminum or its diethyl ether adduct in dry petroleum ether, containing 0.1 mol of the aluminum compound, was added to a gently-refluxing 30 wt % solution of ketone (0.1 mol) in dry petroleum ether. A gaseous product which evolved during the addition of the aluminum compound solution was led through a gas meter to a gas receiver. The reaction solution was then refluxed for an additional 0.5 hr, by which time the gas evolution practically terminated. The reaction solution was cooled in an ice bath, and the aluminum compound was decomposed by adding diethyl ether containing a theoretical amount of water. After the addition of cracked ice, precipitated aluminum hydroxide was removed by filtration and the filter cake was washed thoroughly with ether. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed by distillation using a Widmer column (30 cm), and the residue was then distilled. The components of the distillate were determined by the methods described in the "Analytical Procedure" section, while the residue of the distillation was weighed and its active hydrogen content determined.

Reaction of Acetone with Triethylaluminum. A rectification of the product obtained from the reaction

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1) H. Gilman and K. E. Marple, *Rec. trav. chim.*, **55**, 133 (1936).

2) H. Meerwein, G. Hinz and H. Majert, *J. prakt. Chem.*, (2), **147**, 226 (1937).

3) K. Ziegler, K. Schneider and J. Schneider, *Ann.*, **623**, 9 (1959).

4) G. Wittig and O. Bub, *ibid.*, **566**, 113 (1950).

5) S. Pasynkiewicz and E. Sliwa, *J. Organometal. Chem.*, **3**, 121 (1965).

6) H. Iddles and C. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454, (1934).

7) S. Siggia, "Quantitative Organic Analysis *via* Functional Group," 2nd Ed., John Wiley & Sons, Inc., New York (1954), p. 11.

8) " Micromethods of Quantitative Organic Analysis," 2nd Ed. (1942), p. 263.

of acetone (5.8 g) with triethylaluminum yielded the following three fractions:

Fraction 1 bp 75—78°C, 0.6 g
Fraction 2 bp 95—98°C, 2.0 g
Fraction 3 bp 70—75°C/25 mmHg, 2.2 g

3,5-Dinitrobenzoates of Fraction 1 (mp 121—122°C, from ethanol) and Fraction 2 (mp 116—117°C, from ethanol) were identified as those of isopropyl alcohol and dimethylethylcarbinol, respectively, by mixed-melting-point determinations with the authentic substances. The Fraction 3 was converted into its 2,4-dinitrophenylhydrazone (mp 202—203°C, from ethanol, undepressed by admixture with the authentic hydrazone of diacetone-alcohol).

Reaction of Acetophenone with Triethylaluminum-diethyl ether Adduct. A crude product obtained from the reaction of acetophenone (8.2 g) with the triethylaluminum-diethyl ether adduct was separated by vacuum distillation into a low-boiling fraction (bp 85—95°C/5 mmHg, 6.5 g) and a high-boiling condensation product (bp 195—197°C/5 mmHg, 2.0 g). The low-boiling fraction, after its secondary alcohol content had been determined, was esterified by refluxing it with a solution of phthalic anhydride in dry pyridine containing a slightly excessive amount of anhydride. The tertiary alcohol fraction (3.8 g) was collected by the distillation of the reaction mixture, while the secondary alcohol (0.6 g) was recovered by the hydrolysis of the monoester of phthalic acid obtained as the residue of the distillation. No depression in the melting points of the 3,5-dinitrobenzoate of the secondary alcohol fraction (mp 94—95°C, from ethanol) or in the *p*-nitrobenzoate of the tertiary alcohol fraction (mp 99.0—99.5°C, from ethanol) was observed upon admixture with authentic derivatives of phenylmethylcarbinol and phenylmethylethylcarbinol respectively. The melting point of the semicarbazone (mp 150—151°C, from methanol) of the high-boiling condensation product (bp 195—197°C/5 mmHg) corresponded with that reported for the semicarbazone of dypnone.[9]

Results and Discussion

The results obtained in the reactions of ketones with triethylaluminum and its diethyl ether adduct are cited in Tables 1 and 2.

The reaction of methyl ketone with triethylaluminum with a ketone/AlEt$_3$ mole ratio of 1 and at the temperature of 50—60°C gave considerable quantities of condensation products. The yields of these condensation products in eight experiments, but not with pinacoline, were about 50 wt% based on the ketones used. These high-boiling products appear to be produced by the enolization condensation

TABLE 1. REACTIONS OF TRIETHYLALUMINUM WITH METHYL KETONES

		Reaction product							
Methyl ketone	mol	Condensation prod.		Ethane (mol)	*s*-Alcohol		Ethylene (mol)	*t*-Alcohol %	Recovered ketone
		g	active H (mol)		%	(mol)			
CH_3CO-CH_3	0.100	2.2	0.019	0.019	17.4	0.017	0.017	44.7	0
-C_2H_5	0.082	2.8	0.021	0.026	25.2	0.021	0.022	27.3	0
-C_3H_7-*n*	0.073	3.2	0.019	0.024	14.9	0.011	0.011	34.3	0
-C_3H_7-*i*	0.052	2.2	0.013	0.042	40.8	0.021	0.019	10.4	0
-C_4H_9-*s*	0.078	5.5	0.009	0.028	25.1	0.020	0.019	4.4	0
-C_4H_9-*t*	0.062	0.1	0.001	0.049	39.1	0.024	0.025	59.3	0
-C_5H_{11}-*n*	0.078	4.3	0.019	0.020	31.6	0.025	0.024	20.1	0
-C_5H_{11}-*i*	0.086	2.8	0.012	0.018	20.2	0.017	0.015	51.2	0
-C_6H_5	0.073	4.7	0.017	0.016	46.6	0.034	0.036	0	trace

TABLE 2. REACTIONS OF TRIETHYL ALUMINUM DIETHYL ETHER ADDUCT WITH METHYL KETONES

		Reaction product							
Methyl ketone	mol	Condensation prod.		Ethane (mol)	*s*-Alcohol		Ethylene (mol)	*t*-Alcohol %	Recovered ketone
		g	active H (mol)		%	(mol)			
CH_3-CO-C_2H_5	0.073	1.0	0.007	0.054	10.8	0.008	0.008	70.4	0
-C_3H_7-*i*	0.078	0.3	0.002	0.048	15.6	0.012	0.013	80.6	0
-C_4H_9-*s*	0.062	0.8	0.008	0.044	16.1	0.001	0.001	71.0	0
-C_4H_9-*t*	0.065	0.2	0.002	0.058	28.5	0.019	0.020	68.4	0
-C_5H_{11}-*n*	0.065	1.5	0.007	0.046	4.5	0.003	0.003	75.2	0
-C_6H_5	0.068	2.0	0.008	0.040	6.1	0.004	0.005	36.9	32.6

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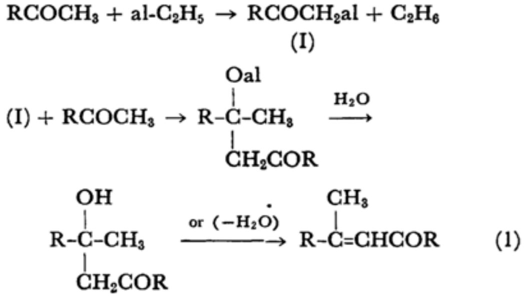
9) N. O. Calloway, *J. Am. Chem. Soc.*, **59**, 809 (1937).

reaction, as is shown in Eq. (1). In fact, in the experiments with acetone and acetophenone, diacetonealcohol and dypnone were obtained respectively. The amounts of ethane in the gaseous products nearly corresponded to that calculated from the active hydrogen content of the condensation products.



$$\mathrm{RCOCH_3 + al\text{-}C_2H_5 \rightarrow \underset{(I)}{RCOCH_2al} + C_2H_6}$$

$$\mathrm{(I) + RCOCH_3 \rightarrow R\text{-}\underset{CH_2COR}{\overset{Oal}{C}}\text{-}CH_3 \xrightarrow{H_2O} R\text{-}\underset{CH_2COR}{\overset{OH}{C}}\text{-}CH_3 \xrightarrow{or\ (-H_2O)} R\text{-}\overset{CH_3}{C}{=}CHCOR} \qquad (1)$$

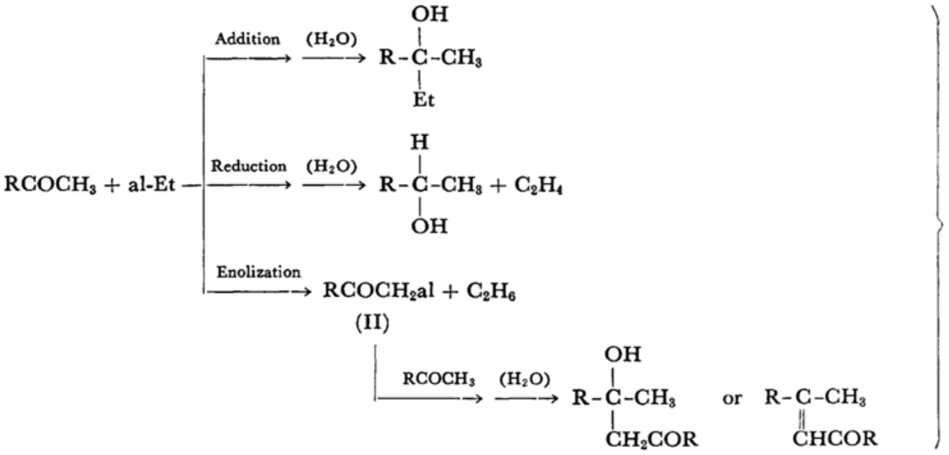
However, in the reaction of pinacoline with triethylaluminum, although considerable quantities of ethane were collected, neither the high-boiling product nor the recovered ketone were obtained; secondary and tertiary alcohols were obtained in yields of 39.1% and 59.3%, respectively. Such an inconsistency between the amount of ethane produced in the course of the reaction and the amount of active hydrogen in the high-boiling condensation product was markedly observed in the case of the reaction with the triethylaluminum diethyl ether adduct.

The reactions of ketone with an equimolar amount of triethylaluminum diethyl ether adduct differ from those with free triethylaluminum; the former afforded a smaller amount of condensation product than the latter. In the experiments with five methyl ketones, but not acetophenone, no ketones were recovered, while the amount of ethane evolved during the reaction was much greater than that obtained from the experiments with free triethylaluminum.

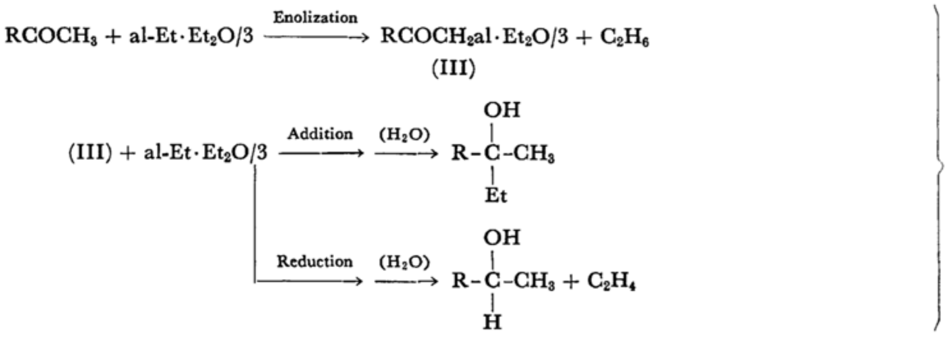
It may be concluded from the results of these experiments that the reaction of methyl ketone with triethylaluminum or its diethyl ether adduct proceeds through the courses indicated by Eqs. (2) and (3).

The enolate (II) produced by the reaction of ketone with free triethylaluminum appears to be so reactive as to react readily with the second molecule of the ketone and thus yield the condensation product. The enolate (III) formed by the reaction of ketone with the diethyl ether adduct of triethylaluminum, however, probably inhibits the condensation reaction because of the blocking effect of the coordinated diethyl ether.[10]

In the case of pinacoline, the reaction with free



$$\mathrm{RCOCH_3 + al\text{-}Et \begin{cases} \xrightarrow{Addition} \xrightarrow{(H_2O)} R\text{-}\underset{Et}{\overset{OH}{C}}\text{-}CH_3 \\ \xrightarrow{Reduction} \xrightarrow{(H_2O)} R\text{-}\underset{OH}{\overset{H}{C}}\text{-}CH_3 + C_2H_4 \\ \xrightarrow{Enolization} \underset{(II)}{RCOCH_2al} + C_2H_6 \\ \qquad (II) \xrightarrow{RCOCH_3} \xrightarrow{(H_2O)} R\text{-}\underset{CH_2COR}{\overset{OH}{C}}\text{-}CH_3 \ \ or\ \ R\text{-}\underset{CHCOR}{\overset{}{C}}\text{-}CH_3 \end{cases}} \qquad (2)$$



$$\mathrm{RCOCH_3 + al\text{-}Et\cdot Et_2O/3 \xrightarrow{Enolization} \underset{(III)}{RCOCH_2al\cdot Et_2O/3} + C_2H_6}$$

$$\mathrm{(III) + al\text{-}Et\cdot Et_2O/3 \begin{cases} \xrightarrow{Addition} \xrightarrow{(H_2O)} R\text{-}\underset{Et}{\overset{OH}{C}}\text{-}CH_3 \\ \xrightarrow{Reduction} \xrightarrow{(H_2O)} R\text{-}\underset{H}{\overset{OH}{C}}\text{-}CH_3 + C_2H_4 \end{cases}} \qquad (3)$$

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10) K. Ziegler, *Ann.*, **629**, 251 (1960).

triethylaluminum affords a sterically-hindered enolate comparable to those produced in the reaction of simple ketone with the triethylaluminum diethyl ether adduct; this is because of the accumulated methyl groups on the α-carbon atom of the carbonyl group. As a result of this steric effect, the addition of the second molecule of pinacoline to the enolate is completely suppressed; thus the reaction does not afford the condensation product.

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