325

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The Reaction between Styrene and Triisobutylaluminum

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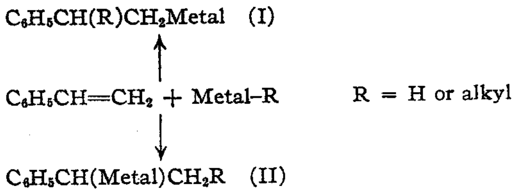
The reactions of styrene with triisobutylaluminum and with dialkylaluminum monohydride have been investigated. Oxidation and hydrolysis of the products of these reactions give 1-phenylethanol and 2-phenylethanol in good yields, as well as small quantities of acetophenone. Moreover, a study of the products obtained from tris-(phenylethyl)-aluminum, obtained in the above reactions with styrene, indicates that about 22–24% of the phenylethyl groups are attached to the aluminum through the carbon adjacent to the phenyl group.

Two isomeric compounds, I and II, have been obtained by the reaction of styrene with organometallic compounds or metallic hydrides.



$$\begin{tikzcd} C_6H_5CH(R)CH_2Metal \quad (I) \\ C_6H_5CH{=}CH_2 + Metal{-}R \arrow[u] \arrow[d] \qquad R = H \text{ or alkyl} \\ C_6H_5CH(Metal)CH_2R \quad (II) \end{tikzcd}$$

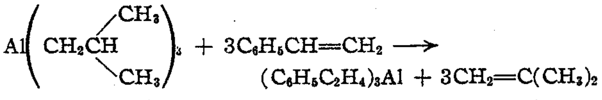
By use of an alkali metal derivative, products of type II predominate[1]; the reaction of trialkyltin hydride to styrene, on the other hand, gives a product of type I.[2]

The reaction of compounds of metals of the third periodic group with styrene has received little attention. Ziegler[3] reported the reaction of styrene with triisobutylaluminum and the oxidation of the product, tris-(phenylethyl)-aluminum, to give 2-phenylethanol. Brown[4] indicated that the same alcohol is obtained by oxidation of tris-phenylethylboron.

This paper presents a study of the reactions of styrene with triisobutylaluminum and with diethylaluminum hydride. The structure and composition of the products have been deduced by oxidation with oxygen, by hydrolysis of the resulting alcoholates, and by analysis of *the phenylethanol* thus obtained by infrared absorption spectroscopy.

Results

The reaction between triisobutylaluminum and styrene was carried out both in the absence and the presence of solvents. Nickel, prepared *in situ* by the decomposition of nickel acetylacetonate, was used as a catalyst.[5]



$$Al\left(CH_2CH(CH_3)_2\right)_3 + 3C_6H_5CH{=}CH_2 \longrightarrow (C_6H_5C_2H_4)_3Al + 3CH_2{=}C(CH_3)_2$$

The tris-(phenylethyl)-aluminum obtained was oxidized at a low temperature (0–25°) but, even at 0°, the reaction does not proceed as smoothly as the oxidation of the trialkylaluminum compounds.[3] The oxidation products include 1-phenylethanol, 2-phenylethanol and acetophenone, using either ether or hexane as a solvent.

Since the secondary alcohol could be produced by isomerization during the oxidation, tris-(1-phenylethyl)-aluminum etherate and tris-(2-phenyl-

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[1] E. Krause and A. von Grosse, "Die Chemie der metall-organischen Verbindungen," Berlin, 1937, pp. 95–96.

[2] G. J. M. van der Kerk, J. G. Noltes and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 356 (1957).

[3] K. Ziegler, F. Krupp and K. Zosel, *Angew. Chem.*, **67**, 425 (1955).

[4] H. C. Brown and B. C. SubbaRao, THIS JOURNAL, **78**, 5694 (1956).

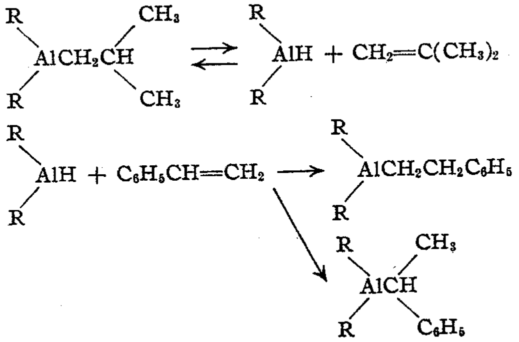
[5] K. Ziegler, H. G. Gellert, K. Zosal, W. Lehmkuhl and W. Pfohl, *Angew. Chem.*, **67**, 424 (1955).

ethyl)-aluminum etherate were synthesized by the method of Krause and Wendt[6] and were oxidized. Moreover, the 1-phenylethylmagnesium chloride and the 2-phenylethylmagnesium chloride used in the syntheses were also oxidized.[7] The 1-phenylethyl compounds gave 1-phenylethanol and traces of acetophenone; the 2-phenylethyl compounds gave 2-phenylethanol but no carbonyl products. Thus it would appear (1) that no isomerization occurs during oxidation and (2) that the proportion of 1-phenylethanol and 2-phenylethanol obtained by oxidation indicates the binding of the phenylethyl group to aluminum in tris-(phenylethyl)-aluminum.

The above contentions are also supported by the data of Tables I and II. Table I summarizes the results when tris-(phenylethyl)-aluminum (prepared from triisobutylaluminum and styrene at 80° with a reaction time of 0.5 hour) is oxidized, partially or wholly, at 0°. Table II summarizes the effect of different conditions on the products obtained by the reaction of styrene with triisobutylaluminum.

These results indicate (1) that 22–24% of the phenylethyl groups in the tris-(phenylethyl)-aluminum obtained by the reaction of styrene with triisobutylaluminum are bound to the aluminum by the carbon atom adjacent to the phenyl group and (2) that the ratio of 1-phenylethyl alcohol to 2-phenylethyl alcohol is not dependent on the extent to which the oxidation has been carried out.

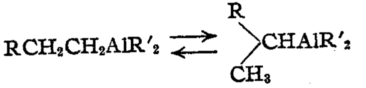
Since the reaction could proceed as



the reaction of styrene with diethylaluminum monohydride has also been studied. Oxidation of the products gave a value of 0.30 for the ratio of 1-phenylethanol + acetophenone/2-phenylethanol, which agrees with the values found for the oxidation products of tris-(phenylethyl)-aluminum obtained from styrene and triisobutylaluminum.

Discussion

The higher proportion of 2-phenylethyl groups in the reaction products may be ascribed to a higher rate of this type of addition. On the other hand, the following equilibrium may be established, where R = alkyl or aryl group



$$\mathrm{RCH_2CH_2AlR'_2} \rightleftarrows \begin{matrix}\mathrm{R} \\ \rangle\mathrm{CHAlR'_2} \\ \mathrm{CH_3}\end{matrix}$$

TABLE I

A: mole of alcohols obtained, expressed as $Al(i\text{-}C_4H_9)_3$ equivalents
B: mole of acetophenone obtained, expressed as in A
C: ratio of moles 1-phenylethanol + moles acetophenone/moles 2-phenylethanol
D: % yield of oxidation products (A and B)

Time, hours	A	B	C	D
0.5[a]	0.359	0.0148	0.24	38
1.5[a]	.560	.0218	.28	58
10.0[b]	.670	.0268	.22	70
16.0[c]	.838	.0954	.28	93

[a] With air. [b] 5 hours with air, then 5 hours with oxygen. [c] 8 hours with air, then 8 hours with oxygen.

TABLE II

A: mole of styrene, expressed as $Al(i\text{-}C_4H_9)_3$ equivalents
B: mole of alcohols obtained, expressed as in A
C: mole of acetophenone obtained, expressed as in A
D: mole of 1-phenylethanol obtained, expressed as in A
E: ratio of moles 1-phenylethanol + moles acetophenone/moles 2-phenylethanol

Syntheses			Oxidation products			
A	Temp., °C.	Time, hr.	B	C	D	E
0.97	20	48	0.631	0.050	0.114	0.318
1.10	80	1	.828	.095	.1235	.310
1.09	80	0.5	.800	.100	.093	.270
1.08	100	0.5	.825	.105	.092	.270

To test this possibility, pure samples of tris-(1-phenylethyl)-aluminum and tris-(2-phenylethyl)-aluminum etherates were heated at 80° in the presence and in the absence of nickel catalyst. The results are summarized in Table III.

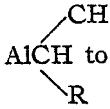
TABLE III

A: mole tris-(phenylethyl)-aluminum etherate
B: mole triethylaluminum
C: mole phenylethanols
D: mole 1-phenylethanol
E: mole acetophenone
F: ratio of moles 1-phenylethanol + moles acetophenone/moles 2-phenylethanol

A	B	Time, hr.	C	D	E	F
0.018[a,c]		24	0.0466	0.0466	0.0034	
.028[a]	0.040	24	.0586	.0230	.0162	1.100
.028[a,c]	.040	24	.0656	.0107	.0073	0.328
.0245[b,c]	.033	100	.0576	.0025	.0071	0.174

[a] Tris-(1-phenylethyl)-aluminum. [b] Tris-(2-phenylethyl) aluminum. [c] With 0.4 mole of Ni-acetylacetonate.

Tris-(1-phenylethyl)-aluminum etherate is stable below 80°, unless it is dissolved in triethylaluminum. In this case, partial isomerization occurs. The value 0.328 in the table is essentially the same as that found for the ratio of products obtained from the reaction of styrene with triisobutylaluminum or with dialkylaluminum hydride.

If, in the reaction with triisobutylaluminum, hexene-1 is used instead of styrene, the $Al(CH_2)_5CH_3$ groups largely prevail, as no appreciable quantities of hexanol-2 have been found in the oxidation of the reaction products, according to Ziegler and co-workers.[8] In other words, the ratio of  $\mathrm{Al}\begin{matrix}\mathrm{CH_3} \\ \mathrm{CH} \\ \mathrm{R}\end{matrix}$ to $AlCH_2CH_2R$ is highly dependent on the nature of the R group: it has a very small value

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[6] E. Krause and B. Wendt, *Ber.*, **56**, 466 (1923).

[7] V. Grignard, *Compt. rend.*, **138**, 1048 (1904); *J. Chem. Soc.*, **86**, I, 494 (1904); see M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, 1954, p. 1264; C. Walling and S. A. Buckler, THIS JOURNAL, **75**, 4372 (1953).

[8] K. Ziegler, H. G. Gellert, H. Martin, K. Nagel and J. Schneider, *Ann.*, **589**, 91 (1954).

when R is aliphatic, but a larger value when R is a phenyl group.

Experimental

Reagents.—Styrene: freshly distilled commercial styrene ($n^{25}_{\rm D}$ 1.5438) was used in all the experiments. *n*-Hexene-1: Phillips pure grade product was used without further purification. Triisobutylaluminum: the commercial product, kindly supplied by the Montecatini Co., was distilled under reduced pressure (0.5 mm.). Analysis of the product was carried out as described by Bonitz[9] and Farina.[10] The purity of the product was 95–98%, the major impurity being diisobutylaminoisobutoxyaluminum. Triethylaluminum: prepared by the reaction of ethylene with triisobutylaluminum, as described by Ziegler[5]; the purity was 93–95%. Diethylaluminum hydride: prepared from triethylaluminum and hydrogen, as described by Ziegler.[5] The product was not isolated but a solution of diethylaluminum hydride in triethylaluminum was used, containing 30% of hydride as determined by the method proposed by Bonitz.[9] 1-Phenylethanol: b.p. 95° (19 mm.), $n^{20}_{\rm D}$ 1.5270, prepared by the procedure of Conant and Blatt.[11] 2-Phenylethanol: b.p. 107° (19 mm.), $n^{20}_{\rm D}$ 1.5311, prepared as described by Huston and Agett.[12] Hexanol-1: prepared by the method of Darick and Bissel[13]; b.p. 156–158° (760 mm.), $n^{20}_{\rm D}$ 1.4194. Hexanol-2: prepared by the method of Pickard and Kenyon[14]; b.p. 140° (750 mm.), $n^{20}_{\rm D}$ 1.4184. Solvents: *n*-hexane, *n*-heptane and benzene were purified by H_2SO_4 treatment, dried by distillation over sodium, and stored under nitrogen.

Analytical Methods.—The quantitative determination of carbonyl groups (acetophenone) was according to Bryant.[15] The quantitative determination of the alcohols was carried out by the method of Petersen.[16] The composition of the mixtures of the isomeric phenylethanols was determined by infrared analysis using the band at 8.32 μ for 1-phenylethanol.[17]

Reaction between Triisobutylaluminum and Styrene and Oxidation of the Reaction Products (Table II, second item).—Nickel acetylacetonate (0.1 g.) was added to a mixture of 40 ml. of *n*-hexane, 41 g. (0.394 mole) of styrene and 24 g. (0.119 mole) of triisobutylaluminum having a purity of 98%. The solution was refluxed for 30 minutes; during this period 8.40 liters of isobutene (corrected to normal temperature and pressure) were evolved. Into the solution, diluted with 30 ml. of hexane and cooled to 0°, air (free from CO_2 and moisture) was bubbled at a rate of 3.5 liters/hour. After 8 hours the air flow was stopped and pure oxygen was bubbled through the solution for another 8 hours.

The oxidation products were then hydrolyzed at 0° by use of 300 ml. of 8% H_2SO_4; the oily products were extracted by ether. After drying with Na_2SO_4, the ether and most of the hexane were evaporated and the residue was analyzed. Acetophenone was identified as the 2,4-dinitrophenylhydrazone (m.p. 243°); authentic specimen, m.p. 245°; mixed m.p. 243°) and quantitatively determined by the hydroxylamine hydrochloride method.[15] By this method 4.07 g. of acetophenone was found. 1-Phenylethanol was identified by oxidizing the reaction products with a stoichiometric amount of CrO_3 in acetic acid after removal of the acetophenone as the 2,4-dinitrophenylhydrazone. 2-Phenylacetaldehyde was removed from the oxidation products by treatment with a saturated solution of $KHSO_3$. 2-Phenylethanol was identified as the *p*-nitrobenzoate (m.p. 63°; m.p. of a mixture with an authentic sample 63°).

The total quantity of 1-phenylethanol and 2-phenylethanol, following the procedure of Petersen,[16] was 36 g. The 1-phenylethanol, determined by infrared analysis as previously described, was 14.9% of the mixture of phenylethanols.

In one instance, the product obtained from 59.5 g. of styrene and 35.9 g. of triisobutylaluminum was divided into four parts; each part was oxidized for a different length of time. The results are summarized in Table I.

Reaction between Diethylaluminum Monohydride and Styrene.—Twenty grams of a mixture containing 5.9 g. (0.069 mole) of $Al(C_2H_5)_2H$ dissolved in $Al(C_2H_5)_3$ was added under nitrogen to 0.13 mole of styrene. The mixture was heated at 100° for 17 hours, cooled to 0°, diluted with 50 ml. of *n*-hexane, and oxidized. After separation of the ethanol, the analysis of the products was carried out as before. 8.07 g. of a mixture of the isomeric phenylethanols, containing 1.77 g. of 1-phenylethanol and 0.83 g. of acetophenone, was obtained.

Reaction between Triisobutylaluminum and Hexene-1.—The method outlined above for the reaction of styrene with triisobutylaluminum was applied to 11.5 g. of 95% $Al(i\text{-}C_4H_9)_3$ (0.0552 mole) and 16 g. (0.19 mole) of hexene-1. After oxidation for 24 hours with air and then 12 hours with oxygen at 20°, 15 g. of pure hexanol-1, as identified by infrared analysis, was obtained. The product gave no test for carbonyl groups.

Synthesis of Tris-(1-phenylethyl)-aluminum Etherate and Tris-(2-phenylethyl)-aluminum Etherate.—Following the Krause and Wendt method,[6] 145 g. (1.03 moles) of 1-chloro-1-phenylethane was treated with 28 g. (1.16 moles) of magnesium suspended in 350 ml. of ether; 50 ml. of the ethereal solution of 1-phenylethylmagnesium chloride gave pure 1-phenylethanol by oxidation with air and oxygen.

An ether solution of 29.3 g. (0.22 mole) of $AlCl_3$ was added to 0.73 mole of an ethereal solution of 1-phenylethylmagnesium chloride. After evaporation of the ether under high vacuum, the tris-(1-phenylethyl)-aluminum etherate was isolated by extraction of the semi-solid mass with benzene. By evaporation of the benzene solution, 97 g. of crystalline, halogen-free solid product was obtained. By oxidizing a benzene solution of the etherate, pure 1-phenylethanol was obtained. No 2-phenylethanol was detected by infrared analysis. Heating a benzene solution of tris-(1-phenylethyl)-aluminum etherate at 80° for 24 hours gave no evidence of isomerization, as demonstrated by oxidation and analysis of the oxidation products.

The synthesis of tris-(2-phenylethyl)-aluminum etherate was carried out as for tris-(1-phenylethyl)-aluminum etherate. The oxidation of the Grignard compound and tris-(2 phenylethyl)-aluminum etherate gave pure 2-phenylethanol.

Isomerization of Tris-(1-phenylethyl)-aluminum Etherate.—The etherate (11.67 g., 0.028 mole) was dissolved in 70 ml. of benzene under nitrogen, and 4.85 g. (0.040 mole) of 94% triethylaluminum and 0.4 g. of Ni acetylacetonate were added. After heating for 24 hours at 80° the reaction products were oxidized and the oxidation products were analyzed. 1-Phenylethanol, 2-phenylethanol and acetophenone were present; the composition of the mixture was 0.875 g. of acetophenone and 8.0 g. of phenylethanols. 1-Phenylethanol accounted for 14.8% of the oxidation products.

Isomerization of Tris-(2-phenylethyl)-aluminum Etherate.—The above conditions, applied to tris-(2-phenylethyl)-aluminum etherate, gave only traces of 1-phenylethanol. When, however, a solution of 10.2 g. (0.0245 mole) of tris-(2-phenylethyl)-aluminum etherate in 60 ml. of benzene was heated for 100 hours at 80°, a larger quantity of 1-phenylethanol, after oxidation, was obtained (Table III, last item).

The composition of the oxidation products was 0.852 g. of acetophenone and 7.03 g. of phenylethanols. 1-Phenylethanol accounted for 3.9% of the mixture.

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[15] W. M. D. Bryant and D. M. Smith, THIS JOURNAL, **57**, 57 (1935).

[16] S. W. Petersen, K. W. Hedberg, B. E. Christensen, *Anal. Chem.*, **15**, 225 (1943).

[17] The authors wish to thank Dr. Domenico Morero who carried out the infrared analyses of the alcohols.