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Reaction of Alkylbenzene. III.[*1] The Reaction of *sec*-Butylbenzene Induced by Aluminum Chloride[*2]

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The products successively obtained from the reaction between *sec*-butylbenzene and aluminum chloride were investigated. Transalkylation was the first observed reaction, followed by the isomerization of the side chain and then by dealkylation. The isomerization of the side chain was observed in the transalkylation products of a high basicity, such as *m*-di- and 1,3,5-tri-substituted compounds, and not in the others. The *n*-butane, resulting from dealkylation, was obtained simultaneously with 2,2di-phenylbutane. On the basis of these results, the reaction mechanism was discussed.

The reaction which alkylbenzenes undergo in the presence of aluminum chloride have been investigated by a number of workers. Transalkylation, dealkylation, and isomerization each having been considered to be a major reaction process in an early step, the reactions have been substantially clarified independently. However, the relations of these three reactions have not yet been reported on except for a few papers.1) In fact, though, all these reaction are so complicated that the obtained products can not be attributed confidently to any reaction process.

In this investigation, the authors investigated the reaction of *s*-butylbenzene induced by aluminum chloride under comparatively mild conditions, and then detected the successive products obtained in the course of the reaction.

Experimental

Materials. *s*-Butylbenzene, which had been ascertained to be fairly pure by vpc analysis, was synthesized by the Friedel-Crafts alkylation of benzene with *s*-butylalcohol at 40°C. The purity of the products decreased at a higher reaction temperature as a result of the isomerization to isobutylbenzene.

The other hydrocarbons used as the authentic materials in vpc analysis were synthesized by the usual methods, except for *n*-butane and isobutane, which were commercially-available chemicals of the highest grade.

All the *s*-butylated benzenes (*p*-di-, *m*-di-, and 1,3,5-tri-*s*-butylbenzene) were synthesized with *s*-butylbenzene and *s*-butyl chloride in the presence of aluminum chloride at a low temperature. These products were not thoroughly pure, but were used satisfactorily for the identification of the individual alkylbenzene in vpc analysis.

2,2-Diphenylbutane was synthesized by the reaction of 2-phenyl-2-butanol with benzene in the presence of aluminum chloride, using the procedure of Serijan and Wise.2) 2-Phenyl-2-butanol, bp 83—85°C/8 mmHg, was prepared by Grignard reaction in a 42% yield based on ethyl bromide using ethylmagnesium bromide and acetophenone. The purity was ascertained by vpc analysis to be more than 90%, and also its NMR spectrum was consistent with its formulation. The reaction of 2-phenyl-2-butanol with excess benzene was carried out at 35°C for 3 hr. The products, bp 150—152°C/3 mmHg, was found by vpc analysis to be slightly contaminated with unknown compounds, but the structure was confirmed by NMR and infrared analyses.

2,3-Diphenylbutane was synthesized by the direct reduction of 2,3-diphenylbutane-2,3-diol, which in turn had been prepared by the Grignard reaction of methylmagnesium bromide and benzil. This diol, bp 165—170°C/7 mmHg, was obtained in a 68% yield based on benzil; it was shown by vpc analysis to be more than 95% pure. The reduction of the diol was carried out in a 100 m*l* autoclave, using hydrogen and copper chromium oxide catalyst in methanol, under a pressure of 150 kg/cm^2 at 150—210°C for 18 hr. The reduction product, bp 112—116°C/2 mmHg, was purified by recrystallization from methanol, and the meso-isomer, mp 125°C, was isolated. (lit.3) mp 127°C). The NMR spectrum of 2,3-diphenylbutane was consistent with its formulation.

The Reaction of s-Butylbenzene. *s*-Butylbenzene (0.3 mol) and aluminum chloride (0.1 mol) were placed in a 100 m*l*, three-necked flask equipped with a stirrer, a thermometer, and a condenser. After stirring, 1 m*l* of the reaction mixture was pippeted out and quenched with cold water. The hydrocarbon layer was then analyzed by vpc. As aluminum chloride was used without any particular treatment, the reaction proceeded

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[*1] Part II; Reference 10.

[*2] Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

1) For example, R. L. Burwell, Jr., and A. D. Shields, *J. Am. Chem. Soc.*, **77**, 2766 (1955); R. M. Roberts, E. K. Baylis and G. J. Fonken, *ibid.*, **85**, 3454 (1963).

2) K. T. Serijan and P. H. Wise, *ibid.*, **74**, 365 (1952).

3) W. T. Somerville and P. E. Spoerri, *ibid.*, **74**, 3803 (1952).

in a heterogeneous system throughout almost all the process.

Analyses of the Products. The products were mainly analyzed by gas chromatography using a Hitachi Model KGL-2 apparatus, fitted with a 90 m, 0.25-mm i. d. capillary column coated with Apiezon grease L or polypropylene glycol (Ucon oil LB-550X) and equipped with a hydrogen-flame ionization detector. Nitrogen was used as the carrier gas, and the operating temperature was varied from 60°C to 190°C according to the boiling points of the samples. Infrared analyses were made with a Shimadzu Model IR-27 apparatus, equipped with a sodium chloride prism. The NMR spectra were taken with a JEOL Model 3H-60 spectrometer at 60 Mc and at room temperature on 10—20% (w/v) solutions of the samples in carbon tetrachloride containing tetramethylsilane as the internal standard.

Results

Identification of Products. A gas chromatogram of all the products obtained from the reaction at 70°C for 3 hr is shown in Fig. 1. In Fig. 1, A, B, and C were identified as *n*-butane, benzene, and *s*-butylbenzene, respectively. The X-group consisted of dibutylbenzenes, of which X_1 and X_4 were identified as *m*- and *p*-di-*s*-butylbenzene with each authentic compound by the internal standard method. It was also considered that X_2 and X_3 consisted of *m*-*s*-butylisobutylbenzene and *m*-diisobutylbenzene, respectively; this consideration was based on the retention volume in vpc and some other evidence, such as the conversion rate shown in Fig. 2 and the existence of an isobutyl group in the following results. The peaks of the Y-group consisted of tributylbenzenes, of which three butyl groups were either *s*- or isobutyl ones substituted at 1,3,5-positions. Y_1 was identified as 1,3,5-tri-*s*-butylbenzene by vpc with an authentic material. Y_2, Y_3, and Y_4 could not be isolated individually. However, the three components were obtained from the reaction products by fractionation; the purity was 94.5% for the three components. The fraction was ascertained to be a mixture of 1,3,5-tri-substituted benzenes on the basis of its infrared spectrum pattern in the 5—6μ region, and was also ascertained to have both the *s*-butyl- and the isobutyl-group in the side chain on the basis of its NMR spectrum,4) which was as follows; $\tau=9.3$ (triplet, γ-methyl-H), $\tau=8.7$ (doublet, β-methyl-H), and $\tau=8.3$—8.5 (multiplet, α-methylene-H) for the *s*-butyl group, and $\tau=9.0$ (doublet, γ-methyl-H) and $\tau=7.4$ (doublet, β-methylene-H) for the isobutyl group. On the basis of this evidence, Y_2, Y_3, and Y_4 were considered to be 1,3,5-di-*s*-butyl-isobutylbenzene, 1,3,5-*s*-butyldiisobutylbenzene, and 1,3,5-triisobutylbenzene respectively. The Z-group consisted of the major products, Z_3 and Z_4, identified as 2,2-diphenylbutane and 2,3-diphenylbutane, respectively by vpc with authentic substances. Some other diphenylalkanes, such as 2-methyl-1,2-diphenylpropane and 2-methyl-1,1-diphenylpropane, were not identified in the peaks of the Z-group.

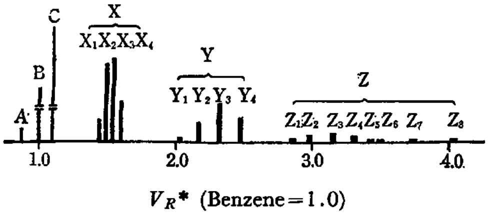

Fig. 1. Gas chromatogram of the reaction products from *s*-butylbenzene induced by $AlCl_3$ at 70°C for 3 hr.

A: *n*-Butane
B: Benzene
C: *s*-Buϕ
X_1: *m*-di-*s*-Buϕ
X_2: *m*-*s*-Bu-*i*-Buϕ
X_3: *m*-di-*i*-Buϕ
X_4: *p*-di-*s*-Buϕ
Y_1: 1,3,5-tri-*s*-Buϕ
Y_2: 1,3,5-di-*s*-Bu-*i*-Buϕ
Y_3: 1,3,5-di-*i*-Bu-*s*-Buϕ
Y_4: 1,3,5-tri-*i*-Buϕ
Z_3: *meso*-2,3-di-ϕ-Butane
Z_4: 2,2-di-ϕ-Butane

Column: capillary (90 m, 0.25 mm i.d.), Apiezon grease L
Temp: 180°C
Carrier: N_2 (Press. 1.5 kg/cm^2)
Detector: F.I.D. (H_2)
* Relative retention volumes

Reaction at 20°C. The yields of the products obtained at 20°C are plotted against the reaction time in Fig. 2.

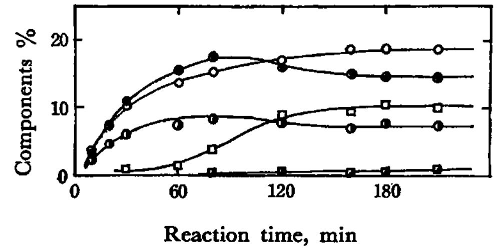

Fig. 2. Reaction product at 20°C.

○ Benzene
⊙ *m*-di-*s*-Buϕ (X_1)
◑ *p*-di-*s*-Buϕ (X_4)
□ 1,3,5-tri-*s*-Buϕ (Y_1)
◪ 1,3,5-di-*s*-Bu-*i*-Buϕ (Y_2) or 1,3,5-di-*i*-Bu-*s*-Buϕ (Y_3)

In the gas chromatogram of the reaction products at 20°C, neither the peak of butane nor that of any Z-component was detected during the first 3 hr. After 260 min, however, the peaks of butane and Z_3 were detected slightly. In the early steps of the reaction, X_1 and X_4 were obtained predominantly; Y_1 was detected 30 min later. The molar ratio of X_1 to X_4 was estimated to be about 2; it kept the same value throughout the reaction course. X_2 and Y_2, each with one isobutyl group,

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4) K. Itoh, S. Hamanaka, F. Yamada and M. Ogawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 914 (1967).

were detected 120 min later, but X_3, Y_3, and Y_4, each having two or three isobutyl groups, were not produced under the present conditions. In the reaction at 20°C, an apparent equilibrium appeared after 180 min.

Reaction at 40°C and 50°C. The X- and Y-groups of reaction products at 40°C and 50°C are shown in Fig. 3 and 4, respectively.

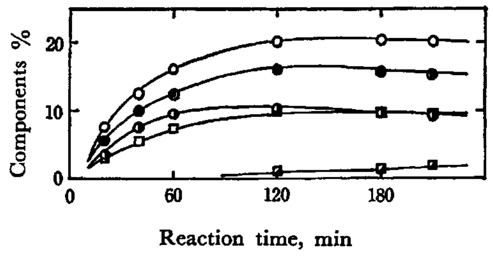

Fig. 3. Reaction products at 40°C.
○ Benzene
⊙ *m*-di-*s*-Buφ (X_1)
◑ *p*-di-*s*-Buφ (X_4)
□ 1,3,5-tri-*s*-Buφ (Y_1)
◪ 1,3,5-di-*s*-Bu-*i*-Buφ (Y_2)
or 1,3,5-di-*i*-Bu-*s*-Buφ (Y_3)

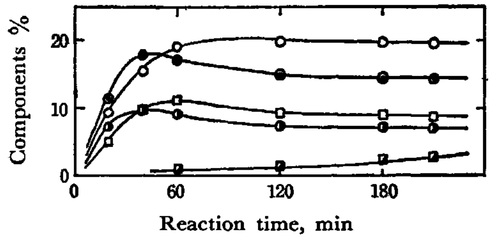

Fig. 4. Reaction products at 50°C.
○ Benzene
⊙ *m*-di-*s*-Buφ (X_1)
◑ *p*-di-*s*-Buφ (X_4)
□ 1,3,5-tri-*s*-Buφ (Y_1)
◪ 1,3,5-di-*s*-Bu-*i*-Buφ
or 1,3,5-di-*i*-Bu-*s*-Buφ (Y_2, Y_3)

These profiles are roughly the same as that of the reaction at 20°C. An apparent equilibrium could be observed after 120 min at 40°C and after 60 min at 50°C. In the latter case, the increase in X_2 and Y_2 were accelerated considerably; then X_1, X_4, and Y_1 decreased.

Reaction at 70°C. The reaction products at 70°C are shown in Fig. 5, with the X-group in the upper figure and the Y-group in the lower one; the Z-group can not be shown precisely because of the difficulty of quantitative determination. In the reaction at 70°C, X_1, X_4, Y_1, X_2, and Y_2 were obtained during the first 10 min, while the A and Z-groups were obtained 20 min later. After these initial reactions, X_3, Y_3, and Y_4, which each possessed two or more isobutyl groups, increased slowly and attained an apparent equilibrium after 180 min.

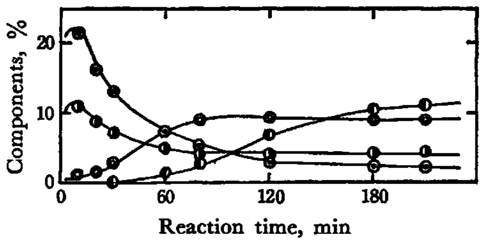

Fig. 5a. Reaction products of X-group at 70°C.
⊙ *m*-di-*s*-Buφ (X_1) ◎ *m*-*s*-Bu-*i*-Buφ (X_2)
◐ *m*-di-*i*-Buφ (X_3) ◑ *p*-di-*s*-Buφ (X_4)

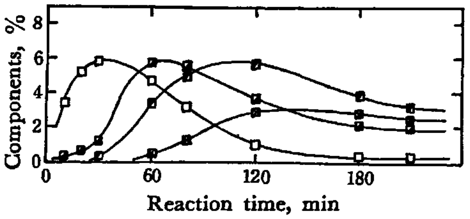

Fig. 5b. Reaction products of Y-group at 70°C.
□ 1,3,5-tri-*s*-Buφ (Y_1)
◪ 1,3,5-di-*s*-Bu-*i*-Buφ (Y_2)
◩ 1,3,5-di-*i*-Bu-*s*-Buφ (Y_3)
⊠ 1,3,5-tri-*i*-Buφ (Y_4)

Discussion

In the reaction of *s*-butylbenzene induced by aluminum chloride at 20°C, transalkylation was the reaction observed first, followed by the isomerization of the side chain and dealkylation. The above reaction sequence was also ascertained at higher temperatures.

Transalkylation > Isomerization > Dealkylation

However, the rate of transalkylation under the present conditions is slower than that of the usual Friedel-Crafts alkylation, in which a reaction equilibrium is completed rapidly, sometimes within a second.5) The present slower reaction rate may be considered to result in part from the heterogeneous reaction and in part from the structure of the attacking species.

The alkylcarbonium ion dissociated from the present reactants may be different from that liberated from alkyl halide in the Friedel-Crafts alkylation. The former ion may be unstable and not so free from the rest; hence, it has a large steric require ment. Consequently, *o*-di-, 1,2,4,-tri-, and 1,2,3-tri-substituted isomers were not obtained among the present reaction products. On the other hand, in alkylation with alkyl halide, the alkylcarbonium ion may be substantially free from paired anions

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5) H. C. Brown and H. Jungh, *J. Am. Chem. Soc.*, **78**, 2182 (1956).
6) G. A. Olah *et al.*, *J. Org. Chem.*, **29**, 2310, 2313, 2315, 2689 (1964).

and can be substituted at the ortho position of alkylbenzene. For the meta-para isomer ratio of alkylbenzene, it has been generally said that the ratio is around 2 : 1, except for the case of a particular alkylbenzene such as di-*t*-butylbenzene.[6] Our present results support the above isomer ratio.

The isomerization of the side chain in which the *s*-butyl group is isomerized to the isobutyl group, which occurred after transalkylation, proceeded to a certain extent. Interestingly, the isomerized products were detected in *m*-di- and 1,3,5-tri-substituted compounds only and not in mono- and *p*-di-substituted ones. In one previous article,[7] the basicities of methylbenzenes were reported to be in the order of the following sequence:

Mesitylene > *m*-Xylene > *p*-Xylene > Toluene

Thus, the present results may be considered to be connected with the basicities of the alkylbenzene concerned. From the above consideration, the relation between transalkylation and isomerization may be represented as in Fig. 6:

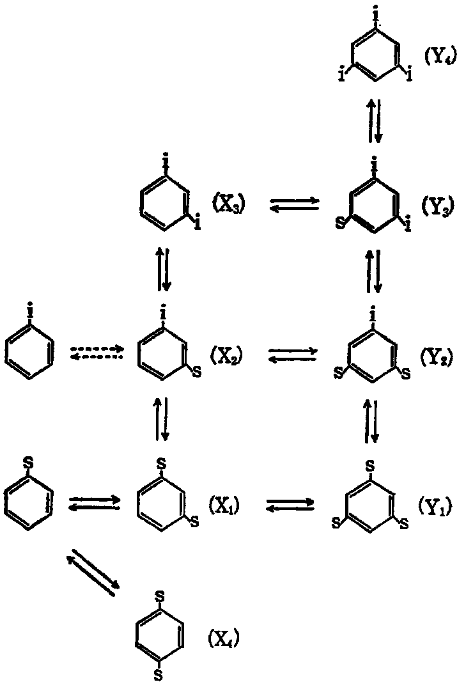
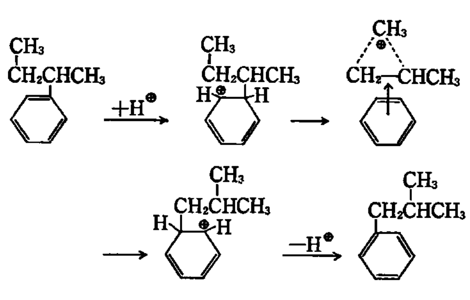
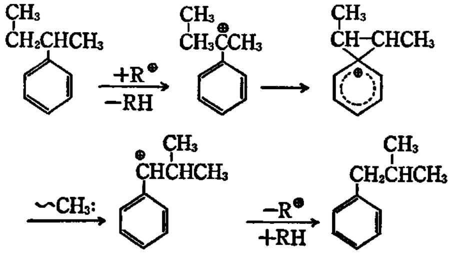


Fig. 6. Route of isomer formation.
s : *s*-butyl group
i : isobutyl group

For the isomerization of such an alkyl group, two mechanisms have been postulated; in one alkylbenzene is coordinated to the proton, isomerized through the methyl-bridged cation,[8] as is shown in Eq. (1), while in the other one the isomerization is initiated by hydride-ion abstraction from the alkyl group and then proceeds *via* a carbonium-ion mechanism, as is shown in Eq. (2).[9]



(1)

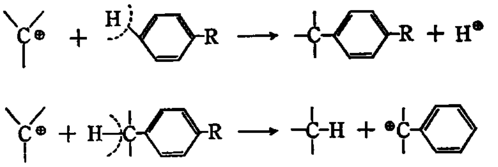


(2)

Our present results support the former mechanism. The latter mechanism can not illustrate how the isomerization in an early step proceeds without the formation of any butane or diphenylbutanes on one side or how *m*-di- and tri-*s*-butylbenzene is isomerized considerably faster than are mono- and *p*-di-*s*-butylbenzene.

Dealkylation was the last reaction in the reaction process. The dealkylation products were detected after 260 min at 20°C and after 20 min at 70°C. In the reaction at 20°C, *n*-butane was obtained simultaneously with 2,2-diphenylbutane (Z_3), while in the reaction at 70°C an unknown compound (Z_2) was first obtained, and then 2,2-diphenylbutane (Z_3), 2,3-diphenylbutane (Z_4) and other Z compounds were obtained succesively.

In a previous paper,[10] we postulated that, in secondary or tertiary alkylbenzene, the dealkylation competed with transalkylation through alkylcarbonium ions.



On the basis of the above results and discussion, the following reaction scheme may be suggested for the formation of 2,2-diphenylbutane:

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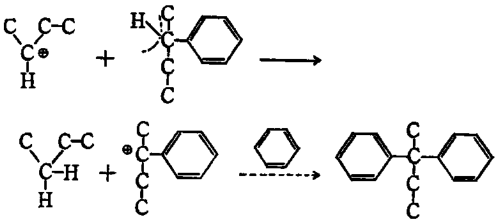
[7] S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 903 (1966).

[8] R. M. Roberts, Y. W. Han, C. H. Schimid and D. A. Davis, *ibid.*, **81**, 640 (1959).

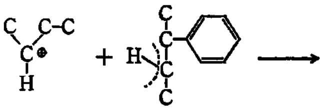
[9] R. M. Roberts and Y. W. Han, *ibid.*, **85**, 1168 (1963).

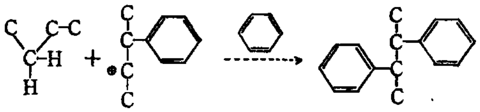
[10] K. Itoh, R. Kurashige, S. Hamanaka and M. Ogawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 918 (1967).



(Z$_3$)

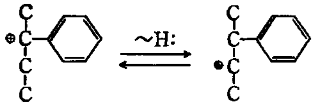
Similarly, the formation of 2,3-diphenylbutane may be described as follows:





(Z$_4$)

In the latter case, another route could also be adopted:



The same discussion may hold for other diphenylbutanes.