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Abstract

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B. V. IOFFE, B. V. STOLYAROV

ON THE ISOMERIZATION AND FRAGMENTATION OF CARBENIUM IONS IN SULFURIC-ACID ALKYLATION

(Presented by Academician O. A. Reutov on 25 IX 1964)

Numerous studies of the Friedel–Crafts reaction have most often been carried out using aluminum halides and other halogen derivatives as catalysts, which are capable of causing secondary reactions, usually the isomerization of the aromatic hydrocarbons formed. For this reason, and also because until recently there were no satisfactory methods for analyzing mixtures of isomeric hydrocarbons, the role of rearrangements of aliphatic carbenium ions in Friedel–Crafts type reactions has remained unclear. To clarify this question we studied the isomeric composition of alkylbenzenes obtained by condensation of aliphatic alcohols with benzene in the presence of 80% sulfuric acid, which does not cause isomerization of aromatic hydrocarbons.* Quantitative analysis of the alkylates was carried out by us by gas-liquid chromatography, a method considerably superior in accuracy and efficiency to the chemical and spectrochemical methods previously used for this purpose. The application of the latter to the study of the composition of mixtures obtained in sulfuric-acid alkylation with alcohols made it possible to establish a very deep isomerization of primary alkyl radicals into secondary or tertiary ones ([4–7]) and to detect skeletal isomerization (in alkylation with neopentyl ([8]), *n*-amyl ([7]), and certain higher normal alcohols ([9])).

Since aromatic hydrocarbons are not isomerized by sulfuric acid, it is obvious that the aliphatic carbenium ions formed as intermediates undergo rearrangement ([10,11]). However, the extent of skeletal isomerization of carbenium ions, the possibility of their fragmentation, and the possibility of skeletal straightening remained completely unclear.

Experiments on the alkylation of benzene with alcohols were carried out at 80° under conditions of vigorous stirring of the reagents and a contact time of 4 hr. The optimum ratio of alcohol, benzene, and 80% sulfuric acid previously found in our laboratory was used: 0.03 mole : 0.06 mole : 12.5 ml, which under the adopted conditions gave a preparative yield of the monoalkylbenzene fraction of 60-65%. After separation of the acid and washing with water, the alkylate was subjected to chromatographic analysis without preliminary fractionation.

In doing so, a previously developed method was used for determining small impurities of *n*-alkylbenzenes in mixtures with secondary and tertiary ones ([12]), while separation of mixtures of amylbenzenes, *iso*- and sec.-butylbenzenes was carried out on a 70-meter capillary column with 7,8-benzoquinoline, which ensured complete separation of all hydrocarbons except the pair 3-phenylpentane —2-phenyl-3-methylbutane. The latter hydrocarbon, however, was not present in the alkylates, as was proved

* The absence of isomerization of side chains under the action of concentrated sulfuric acid has been demonstrated for butylbenzene ([1]), sec.-aminobenzenes ([2,3]), and 3-phenylhexane ([3]) from spectral data, and in our experiments—for all amylbenzenes (using gas chromatography).

by the absence of the bands characteristic of it (7, 9, and 10.3 μ) in the infrared spectra recorded on a DS-301 double-beam spectrophotometer. Peaks on the chromatograms were identified with the aid of reference hydrocarbon samples*.

All 14 propyl, butyl, and amyl alcohols were investigated. As was noted earlier ([14]), in alkylation with *n*-propyl and *n*-butyl alcohols, isomerization of the alkyl radical proceeds to 99.65–99.75%, whereas with isopropyl alcohol and tert-butyl alcohol no isomerization is observed at all. The results of determining the isomeric composition of the monoalkylbenzenes obtained in experiments with the other ten alcohols are presented in Table 1.

Table 1

Isomeric composition of monoalkylbenzenes obtained in the alkylation of benzene with alcohols in the presence of 80% sulfuric acid at 80°
(in percent)

Initial alcohol	2-Phenylbutane	2-Methyl-2-phenylpropane	2-Phenylpentane	3-Phenylpentane	2-Methyl-2-phenylbutane
Butanol-2	87.9	12.1			
2-Methylpropanol-1	15.5	84.5			
Pentanol-1			63	18	9
Pentanol-2			59	35.5	5.5
Pentanol-3			62	31.5	6.5
2-Methylbutanol-1			25	12	63

Initial alcohol	2-Phenylbutane	2-Methyl-2-phenylpropane	2-Phenylpentane	3-Phenylpentane	2-Methyl-2-phenylbutane
2-Methylbutanol-4			0	0	100
2-Methylbutanol-3			0	0	100
2-Methylbutanol-2			0	0	100
2,2-Dimethylpropanol			0	0	47*

* In addition, 46.2% tert-butylbenzene and 6.8% sec-butylbenzene are present.

As can be concluded from the data in Table 1, primary carbenium ions under alkylation conditions are extremely unstable and isomerize completely. This fact is consistent with the recently expressed opinion that the *n*-alkylbenzenes obtained in alkylation with aluminum chloride are products of secondary rearrangements of hydrocarbons ([1,15]). It is very interesting that substantial skeletal isomerization already takes place in sulfuric-acid alkylation with secondary and isobutyl alcohols, as well as with 1-, 2-, and 3-pentanols and 2-methylbutanol-1. In the latter case, and in the case of isobutyl alcohol, straightening of the carbon skeleton is observed.

In the experiment with neopentyl alcohol, in addition to tert-amylbenzene, the formation of which was noted by V. N. Ipatieff and co-workers ([8]), butylbenzenes were detected; moreover, their content exceeded 50% of the sum of the monoalkylbenzenes. The formation of large quantities of butylbenzenes from neopentyl alcohol is of special interest, since it indicates that, parallel with skeletal isomerization of the neopentyl cation to the tert-amyl cation, there proceeds a destruction of it to tertiary and sec-butyl cations, not previously detected because of the imperfection of the analytical methods ([8]). Apparently it is the $C_5H_{11}^+$ ion itself, and not the products of its dimerization, that undergoes fragmentation, since the chromatograms contained no peaks of C_{12} hydrocarbons.

The isomeric composition of the amylbenzenes obtained by us corresponds in general outline to the distribution of isomers in the experiments of Streitwieser and co-workers ([16]) in alkylation with amyl alcohols with boron trifluoride. As these authors showed, isomerization with boron trifluoride pro—

* For the characteristics of the 8 specially synthesized amylbenzenes, see ([13]).

proceeds only in a complex with benzene. It seemed of interest to determine whether isomerization under sulfuric-acid alkylation conditions takes place in the complex of the carbenium ion with the aromatic component or prior to its

formation. To this end we carried out experiments under identical conditions with isobutyl alcohol, but without benzene, which was replaced by an equal amount of pure *n*-undecane (incapable of alkylation under these conditions), or with no hydrocarbon at all. Dry hydrogen chloride was passed through the reaction mixture, and the volatile products were absorbed by *n*-heptane in a well-cooled trap and subjected to chromatographic analysis. It was found that in both cases (with the paraffinic hydrocarbon and without it) a mixture of tertiary and secondary butyl chlorides is obtained in the same ratios as those of the corresponding butylbenzenes in the alkylation experiments (Table 1).

Thus, it may be considered proven that, under conditions of sulfuric-acid alkylation, isomerization occurs at the stage of formation of the carbenium ion, before the formation of its complex with the aromatic component.

Leningrad State University
named after A. A. Zhdanov

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CITED LITERATURE

1. R. M. Roberts, I. W. Han et al., *J. Am. Chem. Soc.*, **81**, 640 (1959).
2. R. L. Burwell, A. D. Shields, *J. Am. Chem. Soc.*, **77**, 2767 (1955).
3. G. Kh. Khakimov, I. P. Tsukervanik, *ZhOKh*, **33**, 493 (1963).
4. B. V. Ioffe, Yan Tsan' -si, *ZhOKh*, **33**, 2496 (1963).
5. V. N. Ipatieff, H. Pines, L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).
6. I. P. Tsukervanik, G. Kh. Khakimov, *ZhOKh*, **32**, 1296 (1962).
7. G. Kh. Khakimov, I. P. Tsukervanik, *ZhOKh*, **33**, 495 (1963).
8. H. Pines, L. Schmerling, V. N. Ipatieff, *J. Am. Chem. Soc.*, **62**, 2901 (1940).
9. G. Kh. Khakimov, I. P. Tsukervanik, *Uzb. Khim. Zhurn.*, No. 1, 76 (1963).
10. L. Schmerling, *Ind. and Eng. Chem.*, **45**, 1447 (1953).
11. G. Baddeley, *Quart. Rev.*, **8**, 355 (1954).
12. B. V. Ioffe, B. V. Stolyarov, *Neftekhimiya*, **2**, 911 (1962).

13. B. V. Ioffe, B. V. Stolyarov, *Neftekhimiya*, **4**, No. 3 (1964).

14. B. V. Ioffe, B. V. Stolyarov, *ZhOKh*, **32**, 3452 (1962).

15. C. D. Nenitzescu, *Experientia*, **16**, 332 (1960).

16. A. Streitwieser, D. P. Stevenson, W. D. Schaeffer, *J. Am. Chem. Soc.*, **81**, 1110, 1113 (1959).

Note: Figure translations are in progress. See original paper for figures.