# Corresponding Member of the Academy of Sciences of the USSR **Yu. G. Mamedaliev**, R. A. Babakhanov,

M. N. Mageramov

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## Abstract

## Full Text

Corresponding Member of the Academy of Sciences of the USSR **Yu. G. Mamedaliev**, R. A. Babakhanov,
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# INTRODUCTION OF THE IODOISOPROPYL GROUP INTO AROMATIC HYDROCARBONS IN THE PRESENCE OF SULFURIC ACID

The study of the synthesis reaction of iodoalkylaromatic compounds containing iodine in the side chain is of definite practical and theoretical interest. However, the development of work in this direction has been held back by the absence of an acceptable method for their synthesis. The data available in the literature on the interaction of allyl iodide with benzene to obtain allylbenzene gave no results ([1,2]), and only in one case ([3]) was it possible to isolate some product characterized as allylbenzene. However, the amount of product was very small, and it would hardly have been possible to judge the structure of the compound obtained correctly from two analyses.

We are carrying out a systematic study of the haloalkylation of aromatic compounds with haloalkenes of various structures. In particular, with a large number of aromatic hydrocarbons it has been shown that allyl halides, in the presence of sulfuric acid, react with aromatic hydrocarbons strictly at the double bond, forming halo-isopropyl derivatives of aromatic hydrocarbons containing chlorine and bromine atoms in the $\beta$-position ([4]).

It was established that chlorine, as the more electronegative atom, promotes greater deactivation of the double bond of the haloolefin, as a result of which the formation of a carbonium ion is impeded; in this connection the yield of the corresponding chlorides is in all cases less than the yield of bromides. In the case of the use of allyl bromide, anomalous reaction products were also isolated, in particular 1,2-diphenylpropane, the mechanism of whose formation was considered by us separately.

The present work is devoted to the synthesis of iodine-containing aromatic hydrocarbons with iodine atoms in the side chain, which, as far as we know from the literature, has not been studied.

It is known that the electronegativity of the iodine atom is considerably lower than that of chlorine and bromine atoms. On the other hand, it is known that the character of the carbon–iodine bond (again proceeding from their electronegativity values, which for iodine and carbon are identical and equal to

−2.5) approximately corresponds to the character of the carbon–carbon bond; sometimes one may even assume in this case the existence of reverse polarity:

$$C^{+}Cl^{-} \rightarrow C^{-}J^{+}.$$

For the reasons indicated, allyl iodide should be more active in reactions of sulfuric-acid haloalkylation than allyl chloride and allyl bromide, as has in fact been shown by us experimentally in the present work.

## Experimental Part

Benzene, toluene, ethyl-, isopropyl-, tert-butylbenzene, cyclohexylbenzene, tetralin, and allyl iodide were used as starting compounds. The iodoalkylation of di- and trisubstituted benzenes was reported earlier (5). Ethyl-, isopropyl-, tert-butyl-, and cyclohexylbenzenes were obtained by alkylation of the corresponding aromatic hydrocarbons with ethylene, propylene, isobutylene, and cyclohexene. Allyl iodide was obtained from allyl chloride by the known procedure (6).

All the listed products were used in the reactions in freshly distilled form and had physicochemical constants closely agreeing with literature data.

Table 1

**Alkylation of aromatic compounds with allyl iodide**

| Experimental conditions and characteristics of reaction products | 4 benzene | 3 toluene | 8 ethylbenzene | 9 cumene | 10 tert-butylbenzene | 12 cyclohexylbenzene | 16 tetralin |
|---|---|---|---|---|---|---|---|
| **Taken, g** | | | | | | | |
| Aromatic hydrocarbons | 39.1 | 46.1 | 53.0 | 60.1 | 67.1 | 80.0 | 67.0 |
| $C_3H_5J$ | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 |

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|---|---|---|---|---|---|---|---|
| $H_2SO_4$ | 12.3 | 12.3 | 12.3 | 12.3 | 12.3 | 12.3 | 12.3 |
| **Obtained, g** | | | | | | | |
| Organic layer | 58.2 | 64.5 | 72.0 | 79.3 | 86.0 | 98.2 | 82.8 |
| Acid layer | 13.4 | 14.4 | 13.4 | 12.8 | 14.0 | 14.8 | 15.7 |
| Losses | 0.8 | 0.5 | 0.9 | 1.2 | 0.4 | 0.3 | 1.8 |
| **Composition of the organic layer, %** | | | | | | | |
| Initial aromatic hydrocarbons | 42.5 | 45.8 | 50.7 | 55.8 | 60.6 | 66.6 | 54.0 |
| $C_3H_5J$ | – | – | – | – | – | – | – |
| Alkylation products | 43.2 | 45.7 | 37.3 | 30.5 | 25.8 | 15.8 | 34.2 |
| Intermediate fractions | – | – | – | – | – | – | – |
| Residue | 5.0 | 3.4 | 4.9 | 6.0 | 5.9 | 6.8 | 6.4 |
| Losses | 7.3 | 5.1 | 7.1 | 7.7 | 7.7 | 6.8 | 5.5 |

| Experimental conditions and characteristics of reaction products | 4 benzene | 3 toluene | 8 ethylbenzene | 9 cumene | 10 tert-butylbenzene | 12 cyclohexylbenzene | 16 tetralin |
|---|---|---|---|---|---|---|---|
| **Yield of alkylation products, %** | | | | | | | |
| Based on allyl iodide taken | 82.1 | 91.3 | 78.5 | 67.1 | 58.8 | 41.2 | 75.5 |
| Based on reacted initial feedstock | 74.9 | 84.3 | 75.7 | 68.9 | 65.6 | 47.3 | 74.4 |

Experimental conditions: $t = 10^\circ$, ratio $C_6H_5R : C_3H_5J : H_2SO_4 = 1 : 0.25 : 0.25$, $H_2SO_4$ concentration 94%, duration of the experiment 1 h, duration of stirring 1 h.

The experiments were carried out in a laboratory apparatus described by us earlier (7). The influence of the reaction temperature, the ratio of the reacting components, the amount and concentration of sulfuric acid, and the duration of the experiment on the iodoalkylation process was investigated. The reaction temperature was varied from 0 to 30°, the ratio of aromatic hydrocarbon to allyl iodide from 3 : 1 to 6 : 1, the concentration of $H_2SO_4$ from 92 to 96%, and the duration of the reaction from 1 to 4 h. Sulfuric acid was taken in an amount from 0.5 to 0.125 mole per mole of the aromatic hydrocarbon taken. The most suitable conditions for obtaining maximum yields of iodoalkylaromatic compounds proved to be: reaction temperature 10°, sulfuric acid concentration 94%, its amount 0.25 mole per mole of aromatic compound, and a ratio of reacting components of 4 : 1 with an overall reaction time of 2 h. A decrease in the yield of the target products upon deviation of the indicated parameters from their optimum values reached, in individual cases, 20%. In a number of experiments decomposition of iodine-containing products was observed, up to liberation of free iodine.

The results of experiments on haloalkylation of aromatic compounds with allyl iodide, carried out under the optimum conditions, are summarized in Table 1. As is evident from the data in this table, under the indicated conditions the reaction proceeds smoothly and is accompanied by substantial yields of the target products. It is interesting to note that, in the presence of $H_2SO_4$, in the reaction of benzene with allyl iodide, the latter exhibits considerably greater activity than allyl chloride and allyl bromide, and even than propylene (8). This phenomenon can, it seems to us, be explained by the considerations given in the review part of this work.

In contrast to the chloro- and bromoisopropylation of monoalkyl derivatives of benzene, in which some deviation was observed from the known regularities characteristic of sulfuric-acid alkylation of aromatic hydrocarbons with propylene (the reactivity of alkylbenzenes as a function of the length and structure of the side group, quantit-

**Table 2**

**Physicochemical constants of the synthesized compounds**

| Formulas and names | B.p. (3 mm), °C | $n_D^{20}$ | $d_4^{20}$ | MR found | MR calculated | I, % found | I, % calculated | Yield, % |
|---|---|---|---|---|---|---|---|---|
| $C_6H_5-CH(CH_3)(CH_2I)$ β-Iodoisopropylbenzene | 94–96 | 1,5870 | 1,5459 | 53,57 | 52,96 | 51,51 | 51,62 | 82,1 |
| $CH_3-C_6H_4-CH(CH_3)(CH_2I)$ β-Iodoisopropyltoluene | 108–110 | 1,5820 | 1,4855 | 58,38 | 57,58 | 48,72 | 48,84 | 91,3 |
| $C_2H_5-C_6H_4-CH(CH_3)(CH_2I)$ β-Iodoisopropylethylbenzene | 122–125 | 1,5720 | 1,4273 | 62,74 | 62,20 | 46,10 | 46,35 | 78,5 |
| $C_3H_7-C_6H_4-CH(CH_3)(CH_2I)$ β-Iodoisopropylcumene | 129–132 | 1,5630 | 1,3805 | 67,65 | 66,82 | 43,90 | 44,09 | 67,1 |
| $C_4H_9-C_6H_4-CH(CH_3)(CH_2I)$ β-Iodoisopropyl-*tert*-butylbenzene | 142–145 | 1,5580 | 1,3371 | 72,81 | 71,43 | 41,82 | 42,05 | 58,8 |

| Formulas and names | B.p. (3 mm), °C | $n_D^{20}$ | $d_4^{20}$ | MR found | MR calculated | I, % found | I, % calculated | Yield, % |
|---|---|---|---|---|---|---|---|---|
| $C_6H_{11}-C_6H_4-CH(CH_3)(CH_2J)$ β-Iodoisopropylcyclohexylbenzene | 180–185 | 1,5760 | 1,3559 | 79,64 | 78,47 | 38,45 | 38,71 | 41,2 |
| $C_{10}H_{11}-CH(CH_3)(CH_2J)$ β-Iodoisopropyltetralin | 175–182 | 1,5935 | 1,4470 | 69,9 | 70,29 | 42,05 | 42,33 | 75,5 |

···ratio of ortho-, meta-, and para-isomers), allyl iodide reacts with alkylbenzenes in accordance with the same regularities as propylene. Thus, toluene is alkylated by allyl iodide better than benzene, while the activity of the other alkylbenzenes decreases with increasing length and branching of the side alkyl group; moreover, the principal reaction product is the para-isomer.

As a result of the work carried out, we have proposed a simple and convenient method for the synthesis of aromatic hydrocarbons with an iodine atom in the side chain in a strictly defined position. Seven new compounds, not described in the literature, have been synthesized; their physicochemical constants are given in Table 2.

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