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STUDY OF THE REACTION OF ALKENYLATION AND HALOALKYLATION OF BENZENE BY HALOALLYL COMPOUNDS WITH A CATALYST BASED ON BORON FLUORIDE

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In the literature ([1]-[3]) one can find a small number of studies on the alkylation of benzene and toluene by haloalkenes with aluminum chloride as catalyst.

In our work, allyl chloride and allyl bromide were taken for alkenylation, and as catalyst an active catalyst not previously investigated for this reaction—the complex compound of boron fluoride and orthophosphoric acid—was used. The reaction was carried out by us at atmospheric pressure in a reaction flask with good stirring of benzene with the catalyst, into which the haloallyl was fed over the course of two hours.

Benzene had the following constants: d_4^{20} 0.8790, n_D^{20} 1.510; b.p. 79-80°; allyl chloride, respectively, d_4^{20} 0.9296, n_D^{20} 1.4154; b.p. 45.5-47.5°; allyl bromide: d_4^{20} 1.4050, n_D^{20} 1.4655; b.p. 69-70°. The reaction products of benzene with allyl chloride, after separation from the catalyst, were washed, extracted with ether, dried, and distilled in vacuum (3 mm Hg), (Fig. 1).

Fig. 1. Distillation curve of the products of interaction of benzene with allyl chloride (1) and allyl bromide (2) (molar ratio benzene : haloallyl 2 : 1, experimental temperature 50°)

The fraction boiling at 86-87° at 3 mm Hg, as the main product, corresponded to β-chloroisopropylbenzene. The fraction boiling in the range 117-119° at 3 mm Hg corresponded to 1,2-diphenylpropane, and the fraction boiling

Table 1

Influence of conditions (molar ratio, amount of catalyst, and temperature) on the results of the reaction of allyl chloride with benzene

No. of experiment	T, °C	Molar ratio: benzene	Molar ratio: allyl chloride	Amount of catalyst, %	Obtained, g: β-chloroisopropylbenzene, b.p. 86–87°	Obtained, g: 1,2-diphenylpropane, b.p. 117–119°	Obtained, g: higher alkylbenzene, b.p. 145–175°	Yield of theoretical, %: β-chloroisopropylbenzene	Yield of theoretical, %: 1,2-diphenylpropane	Yield of theoretical, %: higher alkylbenzene
1	50	3	1	20	40	13	5	25.8	6.6	4.3
2	50	2	1	20	51	21	7	32.9	10.7	6.0
3	50	1	1	20	44	13	12	28.3	6.6	10.0
4	50	0.5	1	20	28	04	11	18.0	2.0	9.0
5	50	1	1	30	36	22	22	23.2	11.2	19.9
6	50	1	1	40	40	16	26	25.8	8.1	21.8
7	70	2	1	20	23	3	4	14.8	1.5	3.4
8	25	2	1	20	18	6	6	11.9	3.0	5.1

in the broad temperature range 145–175°, represented secondary reaction products with two and a greater number of allyl chloride molecules. This fraction had the following characteristics: d_4^{20} 1.0509, n_D^{20} 1.5627; average mol.

weight 233; content of unsaturated compounds 4.3%, Cl 20.44% (theoretical for one Cl atom 15-20%). Along with the alkylation products, 1,2-dichloropropane was formed as the result of a secondary reaction, the yield of which was the greater the less benzene was taken. The results of the experiments are given in Table 1.

Table 2

Effect of the molar ratio on the results of the reaction of benzene with allyl bromide at 50°

No. of experiments	Molar ratio: benzene	Molar ratio: allyl bromide	Catalyst amount, %	Obtained, g: 1,2-dibromopropane	Obtained, g: β-bromoisopropylbenzene	Obtained, g: mixture	Obtained, g: polyalkylbenzene	Yield from theoretical: 1,2-dibromopropane	Yield from theoretical: β-bromoisopropylbenzene	Yield from theoretical: mixture	Yield from theoretical: polyalkylbenzene
1	2	1	20	28	112	26	–	12.8	56.2	13.2	–
2	1	1	20	40	41	09	17	19.8	20.6	4.6	10.0
3	0.5	1	20	46	60	–	29	22.7	30.1	–	18.1

The effect of temperature on the yield of the alkenylation products was also investigated. At 70° a considerable amount of hydrogen chloride is evolved and resinous products are formed.

In all experiments, 1 mole of allyl chloride (77 g) and the corresponding amount of benzene, depending on the number of moles, were taken. Experiments on the alkenylation of benzene with allyl bromide were carried out under analogous conditions.

Fig. 2. Infrared spectrum of β-bromoisopropylbenzene

The alkylate was distilled into the following fractions at 3 mm Hg (Fig. 1).
I –at 41-45° –corresponds to 1,2-dibromopropane.
II –at 95-97° –corresponds to β-bromoisopropylbenzene.
III –at 110-140° –is a mixture of β-bromoisopropylbenzene and 1,2-diphenylpropane.
IV –at 170-195° –polyalkylate, which is obtained when benzene is not taken in excess.

Fig. 3. Infrared spectrum of the polyalkylate in the alkylation of benzene with allyl chloride

The polyalkylate obtained had the following characteristics: d_4^{20} 1.2142, n_D^{20} 1.5743, average molecular weight 280, content of unsaturated compounds 38%, Br 27.4% (theoretical for one Br atom 28.50%). The results of the experiments are given in Table 2.

In order to establish the structure of the synthesized β-chloroisopropylbenzole and β-bromoisopropylbenzene, they were subjected to dehydrohalogenation. As a result, α-methylstyrene was obtained with the following constants: $d_4^{17.4}$ 0.9196; $n_D^{17.4}$ 1.5383; b.p. 52-54°/14 mm (literature data: $d_4^{17.4}$ 0.9134; $n_D^{17.4}$ 1.5384; b.p. 54.5-55°/14 mm).

Oxidation of β-chloroisopropylbenzene and β-bromoisopropylbenzene was carried out by heating them with an aqueous solution of $KMnO_4$. Benzoic acid was obtained as a result. M.p. 120-121°. Spectral analysis in the infrared region showed the presence in the spectrum of these compounds of a strong band at 760 cm^{-1}, corresponding to a structure of the type

$$\underset{\text{phenyl}}{\mathrm{C_6H_5}} - \mathrm{CH(CH_3)} - \mathrm{CHX_2}$$

(Fig. 2). The physicochemical constants and elemental analysis of the products obtained were determined. The results are given in Table 3.

For the polyalkylate, infrared-spectrum data showed that this fraction consists of monosubstituted benzene with a substituent longer than the chloroisopropyl group, with an admixture of other substituted benzenes. Bands for the *o*-, *m*-, and *p*-isomers are absent from the spectrum (Fig. 3).

Thus, on the basis of the work performed, it may be said that the first stage of the interaction of benzene with allyl chloride or allyl bromide in the presence of boron fluoride consists in the formation of the corresponding

Table 3

Obtained substance	B.p., °C/mm Hg found	B.p., °C/mm Hg lit.	d_4^{20} found	d_4^{20} lit.	n_D^{20} found	n_D^{20} lit.	Mol. wt. found	Mol. wt. lit.	MR found	MR calc.	Found, % C	Found, % H	Found, % X	Calculated, % C	Calculated, % H	Calculated, % X
β-Chloroisopropylbenzene, $H_3C-CH(C_6H_5)-CH_2Cl$	86–87/3 mm	85/13	1.0461	1.0471	1.5241	1.5245	155.5	155	45.024	45.360	70.55	7.46	22.80	69.67	7.09	22.95
β-Bromoisopropylbenzene, $H_3C-CH(C_6H_5)-CH_2Br$	95–97/3 mm	78/1	1.3111	1.3120	1.5491	1.5472	200	199	47.924	48.315	55.55	5.62	39.53	54.74	5.52	40.17
1,2-Diphenylpropane, $CH_2(C_6H_5)-CH(C_6H_5)-CH_3$	117–119/3 mm	280–282/atm	0.9910	0.9851	1.5611	1.5635	195	196	64.266	64.132	91.08	9.00	–	91.88	9.18	–
1,2-Dichloropropane, $CH_2Cl-CHCl-CH_3$	96–98/atm	97–98/atm	1.1632	1.1656	1.4939	1.4388	115	113	25.782	24.909	31.01	5.20	61.98	31.85	5.31	62.83
1,2-Dibromopropane, $CH_2Br-CHBr-CH_3$	41–45/3 mm	138–140/atm	1.924	1.9331	1.5199	–	200	202	31.583	32.001	17.31	2.83	78.87	17.82	2.97	79.20

Note. Bromine content in all fractions is 0.

β-haloisopropylbenzene; allylbenzene is not formed:

$$C_6H_6 + CH_2{=}CH-CH_2X \xrightarrow{H_3PO_4\cdot BF_3} C_6H_5-CH(CH_3)-CH_2X$$

A secondary reaction is possible in the following directions:

[[unclear: reaction scheme showing secondary transformations of $C_6H_5CH(CH_3)CH_2X$ with benzene and allyl

The secondary reaction with formation of compounds 2 and 3 and migration of the halogen atom is more probable than formation of compound 1. Alkylation at the tertiary atom of the side chain of alkylbenzenes usually does not occur.

However, no dihalogen derivatives are contained in the reaction products; therefore, the reaction subsequently proceeds with elimination of one halogen atom in the form of HX. Further elimination of halogen from compounds 1′ and 2′ is impossible, and from 3′ is difficult. The formation of 1,2-diphenylpropane has been established; compounds 2 and 3 are obtained as mixtures with other side products of the reaction, and it was not possible to isolate them in pure form. The hydrogen halide acid formed reacts with allyl halide to form dihalopropane.

This direction of the reaction is also confirmed by infrared spectra, by the absence in the spectrum of *o*-, *m*-, and *p*-substituted products, and by analyses of the products of primary and secondary alkylation, containing one alkyl group and one chlorine atom per molecule. The reaction of benzene with allyl bromide proceeds analogously; unsaturated products are obtained in much larger amounts than with allyl chloride, as is confirmed by the high yield of 1,2-dibromopropane (12.8–22.7%). This is apparently connected with the fact that bromine is eliminated more readily than chlorine.

Thus, we have studied for the first time the reaction of alkenylation and haloalkylation of benzene with allyl chloride and allyl bromide using catalysts based on boron fluoride. It has been established that, in the alkenylation of benzene, the reaction proceeds with formation of β-chloroisopropylbenzene, β-bromoisopropylbenzene, and with formation of 1,2-diphenylpropane, but to a lesser extent. In the secondary interaction of β-haloisopropylbenzene with allyl halide, a new reaction, not previously reported by anyone, takes place: growth of the side chain, with one halogen atom remaining in the side chain and, simultaneously, 1,2-dihalopropane being formed.

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