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Abstract

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ALKYLATION OF *p*-DICHLOROBENZENE, *p*-CHLOROBROMOBENZENE, AND *p*-DIBROMOBENZENE WITH PROPYLENE IN THE PRESENCE OF SULFURIC ACID

There are numerous works in the literature devoted to the study of orientation and reactivity in the benzene ring in reactions that are quite widespread in organic chemistry. Unfortunately, these questions have been insufficiently studied for so common a reaction in present-day organic synthesis as the alkylation reaction, especially in cases involving the competing action of several substituents. However, elucidation of the dominant influence of one of the substituents, depending on their electronegativities or size, is of not only theoretical but also definite practical interest for the synthesis of alkyl derivatives of a whole series of functionally substituted aromatic compounds.

In order to fill this gap, we undertook a study of the reaction of alkylation of a series of dihalobenzenes with propylene in the presence of sulfuric acid. Compounds were selected in which two substituents in the benzene ring are in the para position relative to one another and have close electronegativity values (for mutual compensation of their influence on electronic displacements in the benzene ring), but different sizes: *p*-dichlorobenzene, *p*-chlorobromobenzene, and *p*-dibromobenzene. The last two compounds were synthesized by bromination of chlorobenzene and benzene. Alkylation was carried out by the usual method in the apparatus described earlier (^{1}), at temperatures above the melting points of the starting compounds (52-53, 66-67, and 86-87°, respectively). The alkylation reaction of *p*-dichlorobenzene had been studied earlier (^{2}). In the present work we carried out a detailed study of the reaction of alkylation of *p*-chlorobromobenzene and *p*-dibromobenzene with propylene and investigated the influence of changes in various parameters on the maximum and optimum yield of the monoalkyl derivative. Experiments were carried out for all three compounds under the same conditions in order to compare the reactivity of the benzene ring.

Table 1 gives the conditions for the maximum yield of the monoalkyl derivative for the three compounds.

It should be noted that changing even one of the indicated parameters, as well as disturbing the indicated ratio or increasing the concentration of sulfuric acid (to 95%), leads to a considerable decrease in the stated yield values of the monoalkyl derivative for all three compounds.

The regular decrease in the yield of the monoalkyl derivative in the series: *p*-dichlorobenzene, *p*-chlorobromobenzene, *p*-dibromobenzene, is more convincing when comparing the yields of the monoalkyl derivative in reactions carried out under identical conditions for all three compounds. As such conditions, at a sulfuric acid concentration of 92%, the following were chosen: temperature 90°, reaction duration 2 hours, gas feed rate 3 l/hr. The molar ratio of the reaction components and acid was equal to 1 : 1 : 1.5. Table 2 presents the data from these experiments.

Table 1

Conditions for the maximum yield of the monoalkyl derivative
(Sulfuric acid concentration 92%, ratio halogenobenzene : C_3H_6 : H_2SO_4 = 1 : 1 : 1.5)

Conditions	*p*-$Cl_2C_6H_4$	*p*-$Cl_2C_6H_4$	*p*-$Cl_2C_6H_4$	*p*-$BrClC_6H_4$	*p*-$BrClC_6H_4$	*p*-$BrClC_6H_4$	*p*-$Br_2C_6H_4$	*p*-$Br_2C_6H_4$	*p*-$Br_2C_6H_4$
Temperature, °C	60	60	60	70	70	70	90	90	90
Gas feed rate, L/h	3	3	1.5	3	3	1.5	3	3	1.5
Reaction duration, h	1	2	2	1	2	2	1	2	2

Conditions	p-$Cl_2C_6H_4$	p-$Cl_2C_6H_4$	p-$Cl_2C_6H_4$	p-$BrClC_6H_4$	p-$BrClC_6H_4$	p-$BrClC_6H_4$	p-$Br_2C_6H_4$	p-$Br_2C_6H_4$	p-$Br_2C_6H_4$
Yield of monoalkyl derivative, % of theory, calculated on the amount taken	22.92	21.8	22.94	12.49	12.28	12.55	6.3	6.1	6.3
Yield calculated on the reacted amount, %	73.6	73.5	52.7	74.2	74.2	53.5	75	75	54
Content of monoalkyl derivative in the alkylate, %	22.53	24.82	25.68	13.2	13.8	14.11	6.79	6.71	6.75
Residue	8.14	7.41	11.52	6.81	4.2	7.33	3.96	3.18	6.93

It is known that halogen atoms, when present in the benzene ring, promote the entry of the electrophilic agent into the ortho and para positions relative to themselves and sharply hinder entry into the meta position. In the case of a para-disubstituted benzene ring, when both substituents are identical (Cl or Br), all the remaining four positions are equivalent: both ortho positions with respect to one substituent are meta positions with respect to the same substituent, and vice versa. Therefore, the difference between the yields of the monoalkyl derivative in the cases of paradichlorobenzene and paradibromobenzene can be explained only on the basis of the volumes of the substituents, namely: the reason for the lower yield of the monoalkyl derivative in the case of paradibromobenzene is the steric hindrance to entry of the isopropyl group adjacent to the bromine atom, which is more bulky than the chlorine atom.

Table 2

Yields of the monoalkyl derivative, %	Initial compounds	Initial compounds	Initial compounds
	p-$Cl_2C_6H_4$	p-$ClBrC_6H_4$	p-$Br_2C_6H_4$
Content in the alkylate	12.58	9.60	6.71
Residue on distillation	4.61	4.25	3.18
Yield from theory, calculated on the amount of starting product taken	10.8	8.5	6.1
Yield from theory, calculated on the reacted amount of starting product	57.9	67.4	75.0

Let us note that the yield of the monoalkyl derivative of parachlorobromobenzene occupies an intermediate position. It is of interest to determine the position of the isopropyl group in the nucleus, since two isomers are possible here. From the oxidation product of the monoalkyl derivative, a substituted benzoic acid with melting point 155–156° was identified, which corresponds to 2-chloro-5-bromobenzoic acid. Consequently, the isopropyl group enters the ortho position to the chlorine atom. This is understandable, since the negative inductive effect (−J) of chlorine is greater (although only slightly) than that of bromine (electronegativity of chlorine 3.0, bromine 2.8; bond polarity $\Delta C{-}Cl = 0.5$, $\Delta C{-}Br = 0.3$), while the volume of the chlorine atom is considerably smaller than the volume of the bromine atom; i.e., here pro-

steric hindrance and the effect of electron-withdrawing character act together. The low yield of the alkyl product in the case of *p*-chlorobromobenzene, in comparison with *p*-dichlorobenzene, can be explained by probabilistic factors: in the second case all four free positions are equivalent, whereas in the first there are only two such positions (the ortho positions to the chlorine atom).

It should be noted that the increase in the amount of unreacted starting product, although small, rises in the order given in the tables (the yield from theory is calculated on the basis of the starting product that has reacted). This is probably explained by the increasing difficulty of side reactions (sulfonation, etc.) as the volume of the substituents increases. We also note that the monoalkyl derivatives of *p*-chlorobromobenzene collected at 230–237°, and of *p*-dibromobenzene collected at 242–247°, on repeated distillation boiled completely at 234–236° and 244–246°.

On oxidation of these compounds, substituted benzoic acids were obtained with melting points of 155–156 and 152–153°, respectively. The first value coincides with the melting point of 2-chloro-5-bromobenzoic acid, and the second with the melting point of 2,5-dibromobenzoic acid.

Consequently, the synthesized compounds are 2-chloro-5-bromoisopropylbenzene and 2,5-dibromoisopropylbenzene, respectively, and have the following constants (see Table 3):

Table 3

Compounds	B.p., °C	n_D^{20}	d_4^{20}	Mol. wt.	MR	Halide content, %
2-Chloro-5-bromoisopropylbenzene	234–236	1.5432	1.3710	232.84(233.55)	52.79(53.49)	48.85(49.4)
2,5-Dibromoisopropylbenzene	244–246	1.5640	1.6105	277.1(278.01)	55.49(55.69)	56.58(57.49)

Note. The theoretically calculated values are given in parentheses.

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