Chemistry

Corresponding Member of the Academy of Sciences of the USSR
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Abstract

Full Text

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On Orientation and Reactivity in the Benzene Ring in the Alkylation Reaction of Dichlorobenzenes with Propylene

Previously [1] we showed that in the alkylation reaction of paradihalobenzenes with propylene in the presence of sulfuric acid, steric and probability factors play a decisive role in the substitution of hydrogen by an isopropyl group in the benzene nucleus.

In the present work we studied the alkylation of dihalobenzenes of identical composition but different structure, in order to elucidate questions of orientation and changes in the reactivity of definite positions of the benzene ring in the alkylation reaction under the superposition of the effects of two substituents arranged differently with respect to one another. Naturally, the reactivity of the isomers will not be the same. Indeed, if in 1,4-dichlorobenzene, through the superposition of the favorable—for the entry of an electrophilic reagent—ortho effect of one substituent with the unfavorable meta effect of the other substituent, with equally close adjacency of the free positions to a chlorine atom, equivalence of all the free positions is achieved, then in 1,2-dichlorobenzene, with the same superposition of ortho and para effects with the meta effect, an inequality is obvious between the positions adjacent to chlorine atoms and the positions more remote from them. This follows from the inequality of the ortho and para positions relative to a chlorine atom, which is explained not only by the steric factor, but also by the strengthening of the dynamic effect of conjugation with lengthening of the conjugated chains [2] and by the manifestation of a greater influence of the electronegativity of the substituent on the nearest, i.e., ortho, positions. The inequality of ortho and para positions follows from a number of works, among which one should mention the alkylation of chlorobenzene with propylene [3], where, in the fraction corresponding to monoisopropylchlorobenzene, the content of its ortho and para isomers is in the ratio 1 : 4; this agrees with the values of the rates of attack at definite positions in the nitration of chlorobenzene (given by Ingold [4]), with the conditional assumption that the rate for one definite position of benzene is taken as unity:

0.00 0.03
Cl
0.139
0.00 0.03

Further, if in 1,4-dichlorobenzene only one isomer is possible, and in 1,2-dichlorobenzene, of the two possible isomers ($1,2\text{-Cl}_2\text{-3-R-C}_6\text{H}_3$ and $1,2\text{-Cl}_2\text{-4-R-C}_6\text{H}_3$) the second is more probable, then in 1,3-dichlorobenzene, already of the three possible isomers ($1,3\text{-Cl}_2\text{-2-R-C}_6\text{H}_3$; $1,3\text{-Cl}_2\text{-4-R-C}_6\text{H}_3$ and $1,3\text{-Cl}_2\text{-5-R-C}_6\text{H}_3$), on the basis of the considerations given above, the first is unlikely, mainly because of the steric hindrance of two ortho-positioned chlorine atoms; the third isomer is impossible because of the superposition of the meta effect of both chlorine atoms, and thus the greatest probability falls on the second.

Obviously, by similar reasoning one may also predict an increase in the reactivity of isomers in reactions of electrophilic substi-

···placement in the series: para- < ortho- < meta-. For practical confirmation of the conclusions presented, we carried out a study of the alkylation reaction of three isomeric dichlorobenzenes in the presence of sulfuric acid. The alkylation of para- and orthodichlorobenzene has been reported previously (5). In the present work we made a comprehensive study of the alkylation reaction of metadichlorobenzene with propylene in the presence of sulfuric acid under all parameters, carried out special experiments on the alkylation of all three isomers under identical conditions in order to compare their reactivity, and also established the order of replacement of ring hydrogen by the isopropyl group.

For our experiments, orthodichlorobenzene (b.p. 180–181°, n_D^{20} 1.5520, d_4^{20} 1.3046) and metadichlorobenzene (b.p. 171–172°, n_D^{20} 1.5468, d_4^{20} 1.2881) were synthesized in the laboratory from ortho- and metanitrochlorobenzene, respectively, by successive reduction, diazotization, and the usual completion of the reaction according to Sandmeyer; commercial paradichlorobenzene with m.p. 52–53° was used; propylene was obtained by dehydration of isopropyl alcohol.

The alkylation reaction was carried out by the method described previously (6, 7). Investigation of the alkylation reaction of metadichlorobenzene established that this product undergoes sulfonation to a considerable extent during the reaction, as compared with the other isomers. Likewise, in contrast to the other isomers, together with the monoalkyl derivative a dialkyl derivative was isolated. It was established that the best yield of the monoisopropyl derivative, reaching 36% of theory, is provided by carrying out the reaction at 40° in the presence of 95% sulfuric acid, with a molar ratio of the reaction components and acid of $1 : 1 : 1.5$, a propylene feed rate of 3 liters/hour, and an experimental duration of 2 hours.

Table 1

Yields of alkyl derivative	p-$Cl_2C_6H_4$	o-$Cl_2C_6H_4$	m-$Cl_2C_6H_4$
Content of monoalkyl derivative in the alkylate, %	24.82	29.89	46.34
Content of dialkyl derivative in the alkylate, %	–	–	5.51
Residue after distillation of the alkylate, %	7.41	9.02	5.58
Yield of monoalkyl derivative from theory, calculated on the amount of dichlorobenzene taken	21.80	24.05	32.02* (35.68)
Yield of monoalkyl derivative from theory, calculated on the amount of dichlorobenzene that reacted	73.50	69.53	46.10* (51.37)

* The values of the yield of monoalkyl derivative from theory are given in parentheses with allowance for the dialkyl derivative obtained, assuming formation of the latter by successive alkylation of the monoalkyl derivative.

The results of experiments carried out under identical conditions for all three isomers of dichlorobenzene, with the aim of comparing their reactivity, are given in Table 1. These experiments were conducted in the presence of 92% H_2SO_4 at a $C_6H_4Cl_2 : C_3H_6 : H_2SO_4$ ratio equal to 1 : 1 : 1.5, a temperature of 60°, and a gas feed rate of 3 liters/hour. The experiments lasted 2 hours. It should be noted that these conditions do not provide the maximum yield of alkyl derivative for all three isomers.

The data confirm the conclusions of the theory. In the series of para-, ortho-, and meta-isomers the yield of alkyl derivative increases, and the yield rises sharply on going to the meta-isomer. The yield of monoalkyl derivative from theory, calculated on the amount of dichlorobenzene that reacted, changes in the reverse order. Apparently, this too is connected with the increase in reactivity in the series para-, ortho-, and meta-isomers.

in electrophilic substitution reactions and, as a consequence, activation of side reactions (sulfonation, further alkylation). During distillation, an increase in the residue is observed in this series, and on passing to meta-dichlorobenzene it is possible to isolate diisopropyldichlorobenzene, which also confirms the above.

The analyses and studies of the alkyl derivatives carried out in order to establish their structure (recording of absorption spectra in the infrared region, oxidation with an alkaline solution of potassium permanganate to the corresponding benzoic acids) also confirmed the conclusions of the theory concerning the preferential orientation in one or another isomer of dichlorobenzene. As a result it was established that the isopropyl group in 1,4-dichlorobenzene enters one (any) of the four free positions; the isopropyl group in 1,2-dichlorobenzene likewise enters one position (4 or 5, indifferently), and for these isomers only monoisopropyl derivatives are obtained: 1,4-dichloro-2-isopropylbenzene and 1,2-dichloro-4-isopropylbenzene, respectively. 1,3-Dichlorobenzene, along with the monoisopropyl derivative, gives a certain amount of the diisopropyl derivative; in the monoisopropyl derivative the isopropyl group enters one of two positions (4 or 6, indifferently), and 1,3-dichloro-4-isopropylbenzene is obtained,

Table 2

Characteristics of the compounds	p-$Cl_2C_6H_4$; monoalkyl derivative	o-$Cl_2C_6H_4$; monoalkyl derivative	m-$Cl_2C_6H_4$; monoalkyl derivative	m-$Cl_2C_6H_4$; dialkyl derivative
Fraction, °C	219–225	225–230	220–225	238–243
B.p., °C	220–223	226–228	221–223	239–241
n_D^{20}	1.5345	1.5340	1.5344	1.5280
d_4^{20}	1.1604	1.1656	1.1724	1.1245
Mol. wt.	187.2(189.093)*	188.01(189.093)	187.03(189.093)	228.55(231.174)
Mol. refraction	50.19 (49.895)	49.59 (49.895)	49.62 (49.895)	62.58 (63.749)
Cl content, %	37.09 (37.502)	37.18 (37.502)	37.27 (37.502)	30.45 (30.676)

Characteristics of the compounds	p-$Cl_2C_6H_4$; monoalkyl derivative	o-$Cl_2C_6H_4$; monoalkyl derivative	m-$Cl_2C_6H_4$; monoalkyl derivative	m-$Cl_2C_6H_4$; dialkyl derivative
Frequencies in the absorption spectra** in the infrared region, cm^{-1}	760, 817, 8811737, 1900	761, 815, 885,1739, 1899	760, 815, 872,1738, 1892	865, 1728
Substitution positions in benzene according to the spectra	1, 2, 4	1, 2, 4	1, 2, 4	1, 2, 4, 5
M.p. of the acid obtained by oxidation of the alkyl derivative, °C	153—154	202—203	159—160	278—279
Corresponding acid and tabulated m.p. values, °C	2,5-Dichlorobenzoic acid,154.4	3,4-Dichlorobenzoic acid,201.2, 208—9	2,4-Dichlorobenzoic acid,158, 160, 164	4,6-Dichloroisophthalic acid,280
Synthesized compound	Structural formula shown	Structural formula shown	Structural formula shown	Structural formula shown
Synthesized compound	2,5-Dichloroisopropylbenzene	3,4-Dichloroisopropylbenzene	2,4-Dichloroisopropylbenzene	1,3-Dichloro-4,6-diisopropylbenzene

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* In parentheses are given the values calculated theoretically for the composition and structure of the compounds according to the last line of the table.

** The spectra were recorded by N. Yu. Ibragimov in the laboratory of M. A. Salimov on an IKS-14, for which the authors express their gratitude to them.

and in the diisopropyl derivative—in both positions 4 and 6, giving 1,3-dichloro-4,6-diisopropylbenzene.

The characteristics and structure of the synthesized compounds are given in Table 2.

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