meter by 1/4-in. stainless steel column packed with polypropylene glycol (UCON LB 500-X) supported on diatomaceous earth was used. Thirty milliliters of hydrogen per minute was used for carrier gas. The accuracy of the method was checked by analyzing synthetic mixtures of mono- and dihalobenzenes of known composition. An error of less than ±2 relative % was found for most constituents, not exceeding in any case 5%. The retention times given in Table VI were observed.

Acknowledgment.—We are grateful to Dr. D. Cook for the infrared data.

Friedel-Crafts Isomerization. III. Aluminum Bromide-Catalyzed Isomerization of Bromofluorobenzenes, Bromochlorobenzenes, and Dibromobenzenes

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Water-promoted, aluminum bromide-catalyzed isomerization of bromofluorobenzenes, bromochlorobenzenes, and dibromobenzenes leads to the thermodynamically controlled equilibrium mixtures in the case of the bromofluorobenzenes of 5% *ortho*, 63%-*meta*, and 32% *para* isomer, in the case of the bromochlorobenzenes of 5% *ortho*, 62% *meta*, and 33% *para* isomer and in the case of the dibromobenzenes of 4.5% *ortho*, 62% *meta*, and 33.5% *para* isomer. Isomerization of the *ortho*- and *para*-dihalobenzenes investigated involves a fast, intermolecular *ortho-para* interchange followed by a considerably slower intramolecular 1,2-shift leading to the *meta* isomer. Isomerization of the isomeric *meta*-dihalobenzenes also involves predominantly an intramolecular 1,2-shift mechanism. All isomerizations were accompanied by a certain degree of disproportionation, which however was shown not to affect the isomeric ratios of the dihalobenzenes. Suppressing disproportionation by carrying out isomerizations in the presence of the corresponding mono- and trihalobenzenes (the products of disproportionation) gave unchanged isomeric ratios.

The mobility of the bromine substituent in aromatic compounds in the presence of Friedel-Crafts catalysts has long been known. Kohn and Müller[1] observed that tribromophenol in benzene solution in the presence of aluminum chloride yields phenol and bromobenzene. Leroy[2] found that by heating *p*-dibromobenzene with aluminum chloride the product contained *m*-dibromobenzene and disproportionation products in addition to the starting material. In a similar reaction, Copisarov and Long[3] observed the formation of the *o*-dibromobenzene as well. Bromination of halobenzenes led to inconclusive results as far as the isomer distribution and especially the *meta* isomer content of the dihalobenzene was concerned.[4,5] However, Holleman and van der Linden noticed that the amount of *m*-dihalobenzene formed in the chlorination and bromination of monohalobenzenes in the presence of aluminum chloride increases with increasing reaction time.

Though the isomerization reaction of ring-bonded bromine by the action of Friedel-Crafts catalysts has been investigated in recent years,[6a] no detailed study concerning dibromobenzene is available. The aluminum chloride-catalyzed isomerization of bromochlorobenzenes was investigated by Beman.[6b] No investigation on bromofluorobenzene has been carried out.

Results

The isomerization of bromofluorobenzenes, bromochlorobenzenes, and dibromobenzenes effected by aluminum bromide proceeds rapidly towards the thermodynamicallly controlled equilibrium under relatively mild conditions. The procedure for carrying out the isomerization was similar to that described previously[7] for the disproportionation of bromobenzene by water-promoted aluminum bromide. Mixtures of the dihalobenzenes and aluminum bromide, in a molar ratio of 1:0.1 reacted at 30°. Aluminum bromide instead of aluminum chloride was chosen as a catalyst for the reason that it had a good solubility in the haloaromatics investigated and did not effect halogen exchange of bromine substituents (although it can exchange fluorine and chlorine).

The results of the isomerizations are summarized in Fig. 1–7 showing the relative compositions of the reaction mixtures against the reaction time (taking the sum of the amounts of the three dihalobenzene isomers concerned as 100%). *p*-Bromochlorobenzene and *p*-dibromobenzene were isomerized at 100° because of their high melting point. In both cases the reactions were so fast that only the final compositions corresponding to the thermodynamic

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(1) M. Kohn and N. L. Müller, *Monatsh.*, **30**, 407 (1909).

(2) A. J. Leroy, *Bull. soc. chim.*, **48**, 210 (1887).

(3) M. Copisarov and C. N. H. Long, *J. Chem. Soc.*, 442 (1921).

(4) A. F. Holleman, T. van der Linden, *Rec. trav. chim.* **30**, 328 (1911).

(5) M. A. Mounegrat and C. Pouret, *Compt. rend.*, **129**, 606 (1899).

(6)(a) R. Pajeau and P. Fierens, *Bull. soc. chim. France*, 587 (1949).

(6) (b) T. L. Beman, *J. Org. Chem.*, **27**, 3690 (1962).

(7) G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, *J. Org. Chem.*. Part I, **27**, 3441 (1962).

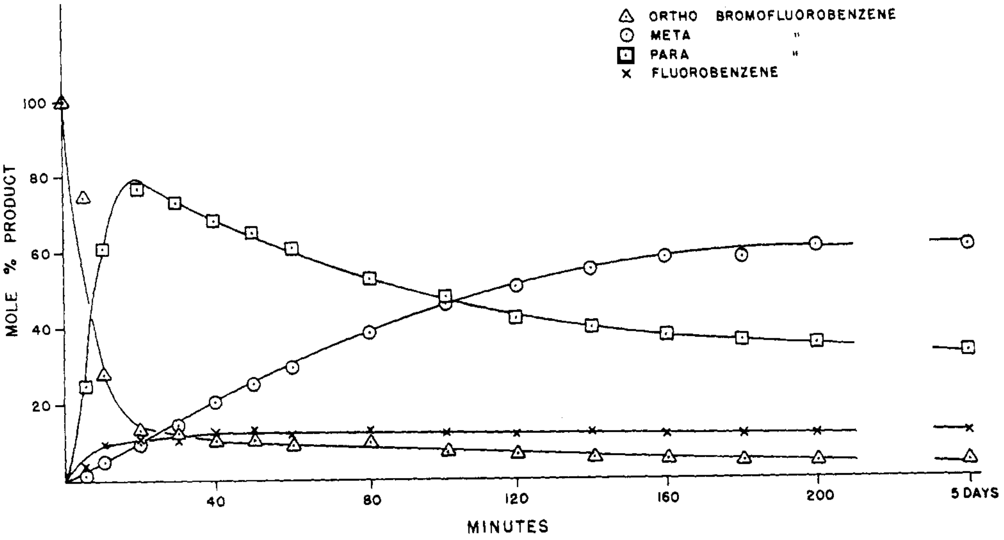


Fig. 1.—Isomerization of *o*-bromofluorobenzene with $Al_2Br_6 + H_2O$ co-catalyst at 30°.

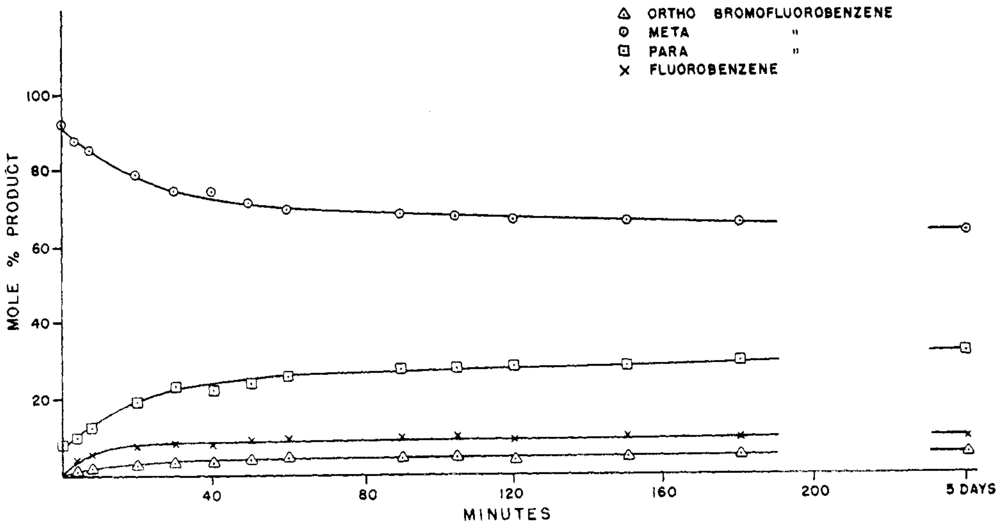


Fig. 2.—Isomerization of *m*-bromofluorobenzene with $Al_2Br_6 + H_2O$ co-catalyst at 30°.

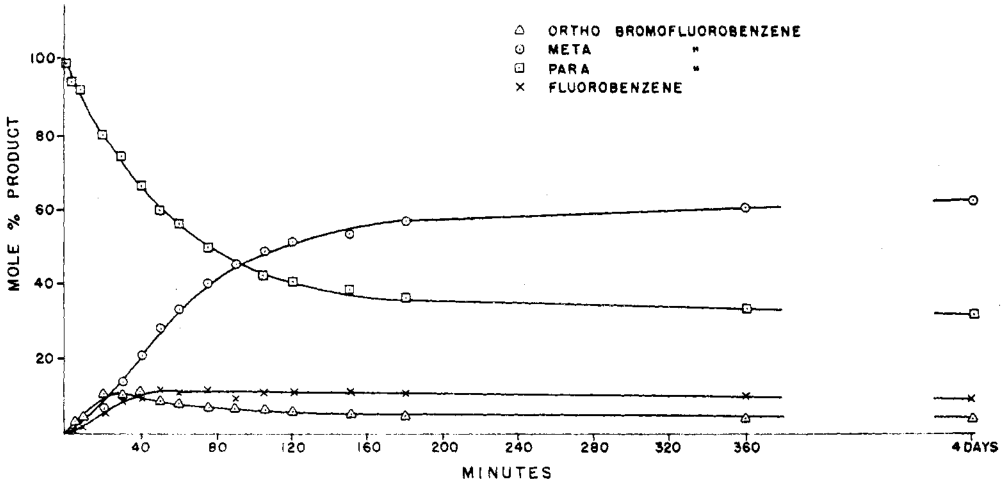


Fig. 3.—Isomerization of *p*-bromofluorobenzene with $Al_2Br_6 + H_2O$ co-catalyst at 30°.

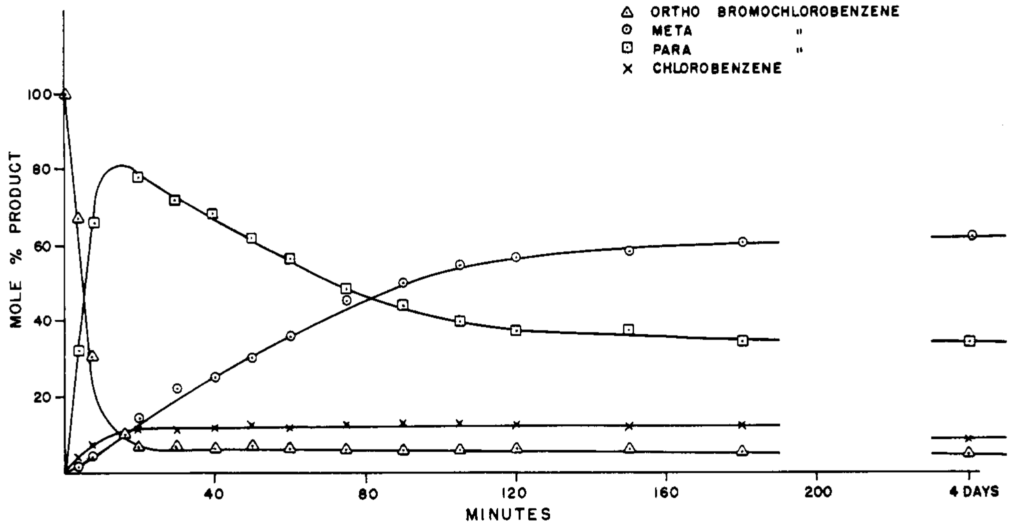


Fig. 4.—Isomerization of *o*-bromochlorobenzene with $Al_2Br_6 + H_2O$ co-catalyst at 30°.

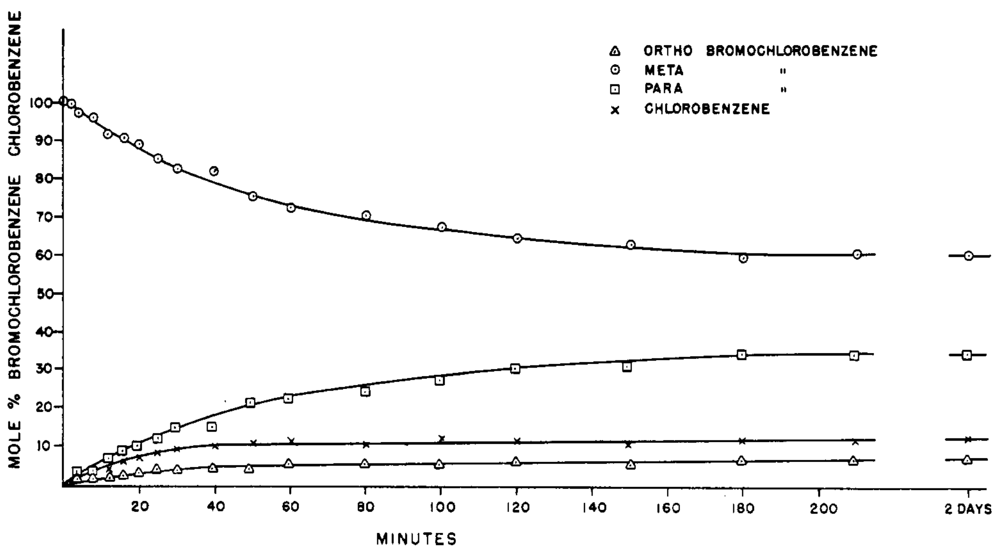


Fig. 5.—Isomerization of *m*-bromochlorobenzene with $Al_2Br_6 + H_2O$ co-catalyst at 30°.

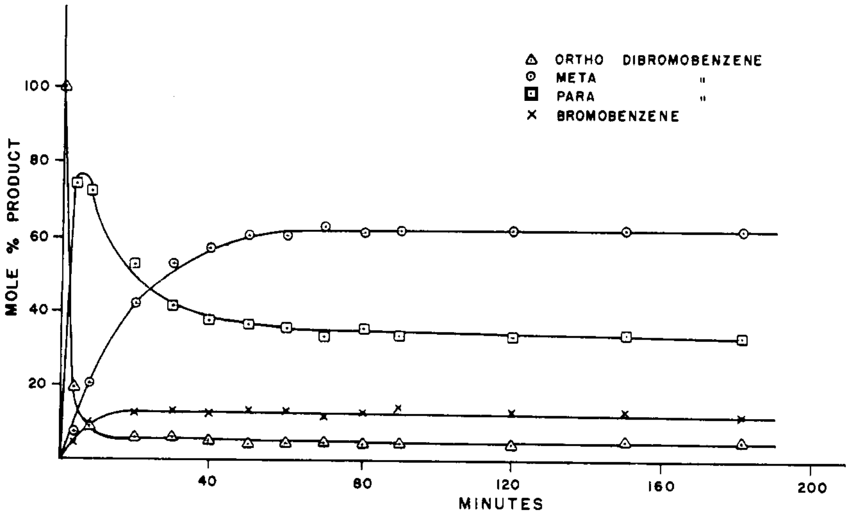


Fig. 6.—Isomerization of *o*-dibromobenzene with $Al_2Br_6 + H_2O$ co-catalyst at 30°.

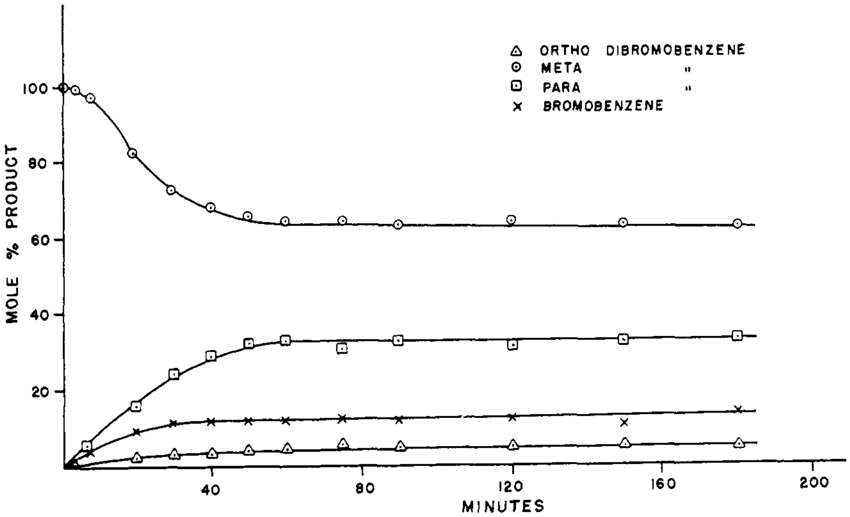


Fig. 7.—Isomerization of *m*-dibromobenzene with Al_2Br_6 + H_2O co-catalyst at 30°.

equilibrium, reached in less than two minutes, could be observed. Equilibrium composition values of these reactions were identical with those of the corresponding *ortho* and *meta* isomers obtained at 30°. The equilibrium compositions obtained were for dibromobenzenes: 4.5% *ortho*, 62% *meta*, and 33.5% *para*; for bromochlorobenzenes: 5% *ortho*, 62% *meta*, and 33% *para*; for bromofluorobenzenes: 5.0% *ortho*, 63% *meta*, and 32% *para* isomer. The practically identical isomer distributions of all three dihalobenzenes suggest that steric hindrance increasing with the size of the second substituent was not a major factor in establishing the equilibrium. To prove that the compositions obtained were indeed the thermodynamically controlled isomer equilibria, synthetic mixtures of approximate compositions were treated with aluminum bromide similarly to the previous experiments. Results as shown in Tables I–III indicate only the expected fast disproportionation reaction yielding mono- and trihalobenzenes (not shown in figures) but no change of isomeric composition of the dihalobenzenes.

TABLE I

TREATMENT OF EQUILIBRIUM MIXTURE OF BROMOFLUOROBENZENES WITH ALUMINUM BROMIDE AT 30°

Time, min.	Fluorobenzene	Bromofluorobenzene *o*-	*m*-	*p*-
0	0	5.6	62.2	32.2
10	10.8	4.9	62.9	32.2
30	11.1	5.2	62.0	32.8
180	11.0	5.4	61.7	32.9

TABLE II

TREATMENT OF EQUILIBRIUM MIXTURE OF BROMOCHLOROBENZENES WITH ALUMINUM BROMIDE AT 30°

Time, min.	Chlorobenzene	Bromochlorobenzene *o*-	*m*-	*p*-
0	0	4.9	61.5	33.6
15	10.2	5.2	62.0	32.8
40	11.6	5.2	61.8	33.0
210	11.9	5.1	61.9	33.0

TABLE III

TREATMENT OF EQUILIBRIUM MIXTURE OF DIBROMOBENZENES WITH ALUMINUM BROMIDE AT 30°

Time, min.	Bromobenzene	Dibromobenzene *o*-	*m*-	*p*-
0	0	4.8	62.4	32.8
15	11.2	4.3	62.8	32.9
30	10.9	4.6	61.7	33.7
100	11.4	4.4	61.7	33.9
140	11.5	4.4	62.3	33.3

That the small amount of water added to the reaction mixture really acted as a co-catalyst (promoter) serving as a proton-source has been proved in comparative experiments. At the same time water added in known amounts as co-catalyst also ensured uniform reaction conditions, regardless of moisture as impurity in the reaction system, the amount of which was unimportant compared with the larger amount of water added in all experiments.

o-Bromofluoro- and *o*-dibromobenzene were treated with aluminum bromide at 30° in the usual manner except that the water co-catalyst has been omitted from the reaction mixture. The results are shown in Fig. 8 and 9.

Comparing the above figures with Fig. 1 and 6 using water as co-catalyst it is seen that the absence of additional water decreased the over-all reaction rates by a factor of about three to five. Complete suppression of the isomerization for lack of proton source has not been expected in these experiments because vigorously anhydrous conditions have not been ensured. Even if it may be possible to obtain absolutely anhydrous reaction conditions, aluminum bromide still could interact with halobenzenes, effecting hydride abstraction and thus providing a source for co-catalyst. However, at lower temperatures this may be a slow process and it could be expected that the rate of isomerization should decrease further.

TABLE IV

ISOMERIZATION OF BROMOFLUOROBENZENES IN THE PRESENCE OF EXCESS BENZENE WITH ALUMINUM BROMIDE AT 30°

Starting material	Time, min.	Fluorobenzene, %	Bromobenzene, %	Bromofluorobenzene, %		
				ortho	*meta*	*para*
o-Bromofluorobenzene	0	0	0.9	99.1	0	Trace
	10	48.9	50.0	Trace	1.1	Trace
	50	48.4	50.3	Trace	1.3	Trace
	180	48.6	50.2	Trace	1.2	Trace
m-Bromofluorobenzene	0	0	0	Trace	99.3	0.7
	4	11.4	11.8	Trace	76.8	Trace
	15	20.2	20.5	Trace	59.3	Trace
	40	26.4	25.2	Trace	48.4	Trace
	90	37.2	39.7	Trace	23.1	Trace
	180	41.7	44.6	Trace	13.7	Trace
	360	48.8	49.0	Trace	2.2	Trace
p-Bromofluorobenzene	0	0	0.5	0	Trace	99.5
	10	47.8	49.6	0	1.5	1.1
	60	48.0	50.1	Trace	1.9	Trace
	180	48.2	50.2	0	1.6	Trace

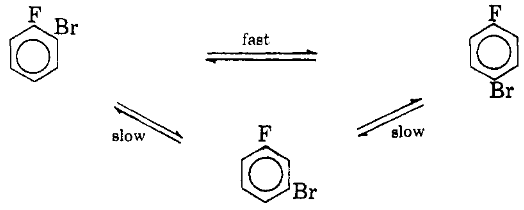
Discussion

Bromofluorobenzenes.—Ring-bonded fluorine is unable to undergo either intra- or intermolecular migration under Friedel-Crafts conditions.[7,8] Therefore it must be concluded that any isomeric changes in bromofluorobenzenes during promoted aluminum bromide-catalyzed isomerization experiments must have involved migration of bromine atoms alone.

As may be seen from Fig. 1 and 3 in the case of the isomerization of *o*- and *p*-bromofluorobenzenes respectively, there is a fast decrease in the concentration of the starting material and a simultaneous fast increase in the amount of the corresponding *para* or *ortho* isomer, without however a rapid change in the amount of *meta* isomer. The fast interchange between the *ortho* and *para* positions leads to a quasi-equilibrium of the two isomeric bromofluorobenzenes with an *ortho-para* ratio of about 1:6.5. This ratio does not change appreciably during the later part of the reaction when the amount of both isomers decreases due to a slower transformation to *meta* isomer.

The fast primary *ortho-para* interchange must be considered as an intermolecular bromine migration. The quasi-equilibrium closely corresponds to the isomer ratio obtained in electrophilic bromination of fluorobenzene. The presence of *meta* isomer does not interfere with the fast *ortho-para* interchange, since a mixture of 62% *m*-bromofluorobenzene and 38% of *o*- or *p*-bromofluorobenzene has shown the same *ortho-para* interchange.

Based on these facts it seems that the *ortho-para* interchange is an independent reaction not influenced by the *meta* isomer in the three-component equilibrium.



Further proof of the intermolecular fast bromine migration step was obtained when the isomerization of bromofluorobenzene with promoted aluminum bromide was attempted in benzene solution. Data in Table IV show that the fast *ortho-para* exchange is completely absent; however, smaller amounts (up to about 2%) of *m*-bromofluorobenzene are formed. The starting *o*- or *p*-bromofluorobenzene isomers rapidly diminished with subsequent formation of bromobenzene (and fluorobenzene). Thus Br^+ was removed in the intermolecular migration step from bromofluorobenzene, brominating excess benzene preferentially over the small amount of fluorobenzene present. *m*-Bromofluorobenzene shows a much slower transbromination of benzene, but after three hours at 30° about 98% is transformed to bromobenzene and fluorobenzene. (In comparisons in the case of *o*- and *p*-bromofluorobenzenes at 30° the transbromination is accomplished in less than ten minutes.)

The transformation of the quasi-stationary *ortho-para* isomer mixture to the equilibrium isomer distribution containing about 63% *meta* isomer (together with 5% *ortho* and 32% *para)* takes place much more slowly than the primary *ortho-para* exchange and involves most probably a 1,2-shift mechanism (intramolecular migration).

A slow 1,2-shift bromine migration must also be effected in the isomerization of *m*-bromofluorobenzene in benzene solution. However the *ortho* and *para* isomers formed themselves rapidly undergo an intermolecular transbromination of benzene and consequently the equilibrium is slowly pushed entirely to bromobenzene and fluorobenzene.

The isomerization of *m*-bromofluorobenzene, as shown in Fig. 2, is also in accordance with a relatively slow, intramolecular 1,2-shift mechanism.

The present experimental technique however

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(8) Investigation of the electrophilic bromination of fluorobenzene was reported by one of us previously [G. Olah, A. Pavlath, and G. Varsanyi, *J. Chem. Soc.*, 1823 (1957)]. A kinetic investigation of a "positive bromine" bromination of halobenzene is being published.

TABLE V

ISOMERIZATION OF BROMOCHLOROBENZENES IN THE PRESENCE OF EXCESS BENZENE WITH ALUMINUM BROMIDE AT 30°

Starting material	Time, min.	Chlorobenzene, %	Bromobenzene, %	Bromochlorobenzene, %		
				ortho	*meta*	*para*
o-Bromochlorobenzene	0	0.0	0.0	100.0	Trace	Trace
	15	47.4	48.6	1.2	2.8	Trace
	30	48.2	49.9	Trace	1.9	Trace
	180	47.9	50.0	0.0	2.1	Trace
m-Bromochlorobenzene	0	0.0	0.0	0.0	100.0	0.0
	15	4.9	4.8	0.0	90.3	Trace
	30	9.5	10.5	0.0	80.0	Trace
	60	20.3	21.1	0.0	58.6	Trzce
	120	28.6	29.9	0.0	41.5	Trace
	180	37.4	39.4	0.0	23.2	Trace
p-Bromochlorobenzene	0	0.0	0.0	0.0	0.0	100.0
	15	47.5	48.1	0.0	2.3	2.1
	30	49.8	48.1	0.0	2.1	Trace
	180	47.5	50.3	0.0	2.2	Trace

does not enable us to draw any conclusions concerning the relative rates of the reactions

meta ⟶ *ortho*

meta ⟶ *para*

Even if the relative rates of interchange were much faster in one case than in the other, the rate of migration between the *ortho* and *para* isomers is so much faster in both directions that the difference would not be noticeable.

Direct formation of the *meta* isomer in an intermolecular step involving electrophilic bromination can not account for the high *meta* ratios, as electrophilic bromination of fluorobenzene yields only a very small amount of *meta* isomer (less than 2%).[8]

Bromochlorobenzenes.—The isomerization of bromochlorobenzenes with water-promoted aluminum bromide catalyst shows a very similar pattern to that of the isomerization of bromofluorobenzenes. Again, a fast *ortho-para* interchange was observed in the isomerization of *o*-bromochlorobenzene (Fig. 4) giving a quasi-stationary *ortho-para* ratio of about 1:6.5. No detailed investigation of *p*-bromochlorobenzene was possible, due to the relatively high melting point of the isomer, which prevented carrying out isomerizations at the usual temperature (30°). At temperatures above the melting point, (68°), the isomerization was too fast to obtain data prior to reaching equilibrium. However the behavior of both *o*- and *p*-bromochlorobenzene in isomerizations with aluminum bromide catalyst in excess benzene solution (Table V) gave results (fast transbromination with simultaneous formation of chlorobenzene) identical to previous observations on *o*- and *p*-bromofluorobenzene. Therefore it is concluded, that in the case of isomerization of *o*- and *p*-bromochlorobenzenes, the fast *ortho-para* conversion represents an intermolecular bromine migration. The fast intermolecular *ortho-para* exchange is accompanied by a considerably slower intramolecular 1,2-shift leading to *m*-bromochlorobenzene. This migration was also observed to a certain degree in the isomerizations carried out in benzene solution.

Isomerization of *m*-bromochlorobenzene (Fig. 5) shows a similar pattern to that of *m*-bromofluorobenzene and is interpreted as an intramolecular 1,2-shift isomerization. Since in this case the chlorine atom also could undergo migration, it can not be stated with certainty, on the basis of experimental data, that the bromine atom constitutes the only migrating group. However the previously investigated isomerization of *m*-chlorofluorobenzene[9] shows such a significant difference in velocity from that of the isomerization of *m*-bromochlorobenzene, that it is difficult to suggest an explanation other than that the migrating group is almost exclusively the bromine atom. (Equilibrium is reached at 30° in less than two hours, while in the case of *m*-chlorofluorobenzene, involving intramolecular chlorine migration, equilibrium is reached only in about seven days at 150°.)

Present data show good agreement with Beman's equilibrium data obtained in aluminum chloride-catalyzed isomerization.[6a]

Dibromobenzenes.—The isomerization of *o*-dibromobenzene (Fig. 6) shows again close similarity with that of *o*-bromofluorobenzene and *o*-bromochlorobenzene. The fast intermolecular *ortho-para* interchange (giving an *ortho-para* ratio of about 1.6.5) is accompanied by a slow 1,2-shift mechanism leading to the thermodynamic equilibrium mixture containing 62% *m*-dibromobenzene (with 4.5% *o*- and 33.5% *p*-dibromobenzene). The intermolecular nature of the fast *ortho-para* exchange is confirmed by the fact that the *ortho-para* ratio (1:6.5) obtained by the fast interchange between these two positions in the present experiments corresponds to the isomer distribution of dibromobenzenes formed by the electrophilic bromination of bromobenzene.

Again the high melting point of *p*-dibromobenzene prevented a detailed investigation of the isomerization of the *para* isomer prior to reaching equilibrium. However isomerization of both *o*- and *p*-dibromobenzene in benzene solution gave evidence of fast intermolecular transbromination, in

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(9) G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, *J. Org. Chem.*, Part II, **27**, 3449 (1962).

accordance with an intermolecular bromine migration from both isomers (Table VI).

TABLE VI

ISOMERIZATION OF DIBROMOBENZENE IN THE PRESENCE OF EXCESS BENZENE WITH ALUMINUM BROMIDE AT 30°

Starting material	Time, min.	Bromobenzene, %	—Dibromobenzene, %— ortho	meta	para
o-Dibromobenzene	0	0.0	100.0	0.0	0.0
	10	96.2	1.7	2.1	Trace
	40	98.4	Trace	1.6	Trace
	120	98.1	0.0	1.9	Trace
	360	98.0	0.0	2.0	Trace
p-Dibromobenzene	0	0.0	0.0	0.0	100.0
	10	95.7	0.0	1.7	2.6
	40	98.5	0.0	1.5	Trace
	120	97.9	0.0	2.1	Trace
	360	97.8	0.0	2.2	Trace

The isomerization of *m*-dibromobenzene (Fig. 7) is in accordance with the similar isomerization of *m*-bromofluorobenzene and *m*-bromochlorobenzene and is interpreted as an intramolecular 1,2-shift isomerization. As some *m*-dibromobenzene was formed in the isomerization of *o*- and *p*-dibromobenzenes in benzene solution (where the intermolecularly migrating positively changed bromine is "captured" by the excess benzene) this again supports the suggestion of the formation of the *meta* isomer by an intramolecular 1,2-shift mechanism. That the *meta* isomer is formed by a different mechanism than the *ortho-para* interconversion is of course also supported by the fact that the amount of *meta* isomer formed in the electrophilic bromination of bromobenzene is very small and can not account for the high *meta* ratios observed in isomerizations.

The rate of formation of the *meta* isomer is not only considerably slower in the isomerization of *o*- and *p*-dibromobenzenes, but the same sequence is also observed in the formation of dibromobenzenes in the disproportionation of bromobenzene under the catalytic effect of promoted aluminum bromide.[7] Disproportionation of bromobenzene with 0.005 and 0.001 molar aluminum bromide catalyst concentrations gave isomer distributions of the dibromobenzene of 12.7% *ortho*, 6.3% *meta*, 81.0% *para* and 13.8% *ortho*, 1.7% *meta*, 84.5% *para*, respectively. In both cases the reactions were carried to about 8% disproportionation.

Disproportionation Accompanying Isomerizations.—All three dihalobenzenes investigated showed not only a strong tendency to undergo isomerization but also disproportionation. As disproportionation must be a consequence of intermolecular halogen transfer, this obviously is taking place involving the bromine substituents. The amounts of monohalobenzenes found in the equilibrium composition of the three dihalobenzenes were practically identical, about 12–13% of the dihalobenzenes present. Trihalobenzenes, dibromofluoro-, dibromochloro-, and tribromobenzenes (not shown in the figures) formed as the products of disproportionation from the corresponding dihalobenzenes were always in a slight excess over the amounts of monohalobenzenes formed in the same reaction. Concentration of the trihalobenzenes was found to be in the range of 13–15%. The relative deficiency in monohalobenzenes, as compared to the trihalobenzenes, may have been caused by such side reactions as arylation leading to the formation of biphenyls and other high molecular weight materials, bromination and polymerization by the catalyst. These reactions indeed were proven in separate experiments—treating halobenzenes and benzene with water-promoted aluminum bromide under the conditions corresponding to those of the isomerizations. Detailed study of the isomer distribution of the trihalobenzenes formed from bromofluoro- and bromochlorobenzenes has not been made. In the case of tribromobenzene the ratio of the 1,2,3-: 1,2,4-: 1,3,5-isomers has been found to be 1:8:5. This however does not necessarily correspond to the thermodynamic equilibrium. No effort was made to investigate higher substituted halobenzenes or other high-boiling compounds and tars. The amount of tarry materials, formed in low temperature reactions is however negligible, since the reaction mixtures obtained from reactions with reaction times as long as one week quenched with water were only slightly colored. On the other hand, products of high temperature reactions (*p*-dibromo- and *p*-bromochlorobenzenes reacted at 100°) had not only an intense yellow-brown color after quenching with water but contained a considerable amount of insoluble carbonaceous material.

In order to establish whether disproportionation has affected the isomerization of dihalobenzenes previously discussed, experiments were carried out under conditions limiting or excluding disproportionation. Disproportionation of dihalobenzenes can be suppressed by adding the products of disproportionation (halo- and trihalobenzenes) to the reaction mixture. In experiments where mixtures of *o*- and *p*-dibromobenzene isomers and 12% bromobenzene were treated with water-promoted aluminum bromide in the usual way, isomeric changes proceeded identically with those shown in Fig. 6 and 7. No change in the relative amount of bromobenzene was observed. Tribromobenzenes formed only in trace amounts during twenty-four hour reaction periods. At the same time these experiments showed that the 12–13% disproportionation found in previous experiments corresponds to the correct equilibrium value.

Isomerization of dibromobenzene in the presence of both bromobenzene and tribromobenzene was also investigated when a mixture of 0.1 mole of *o*-dibromobenzene, 0.2 mole of monobromobenzene, and 0.2 mole of 1,2,4-tribromobenzene was treated with 0.05 mole of Al_2Br_6 and 1 ml. of water in the

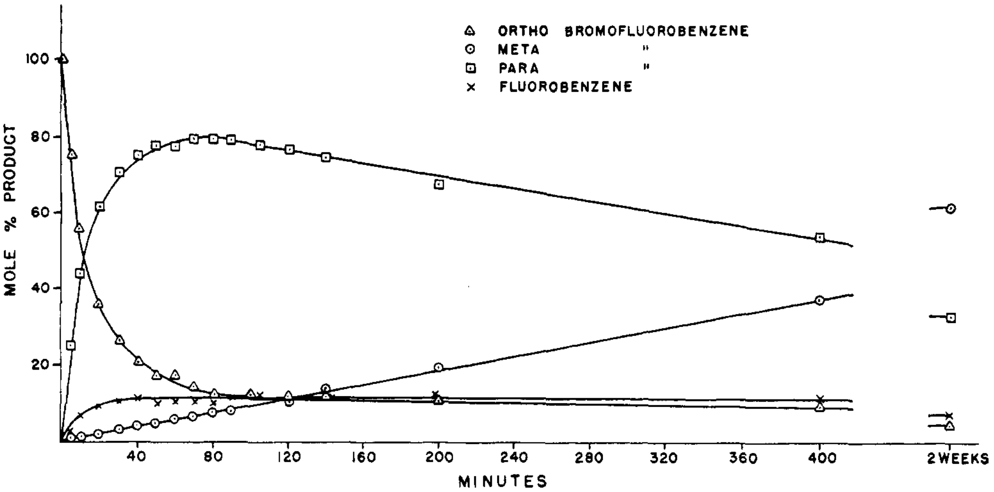


Fig. 8.—Isomerization of *o*-bromofluorobenzene with Al_2Br_6 at 30°.

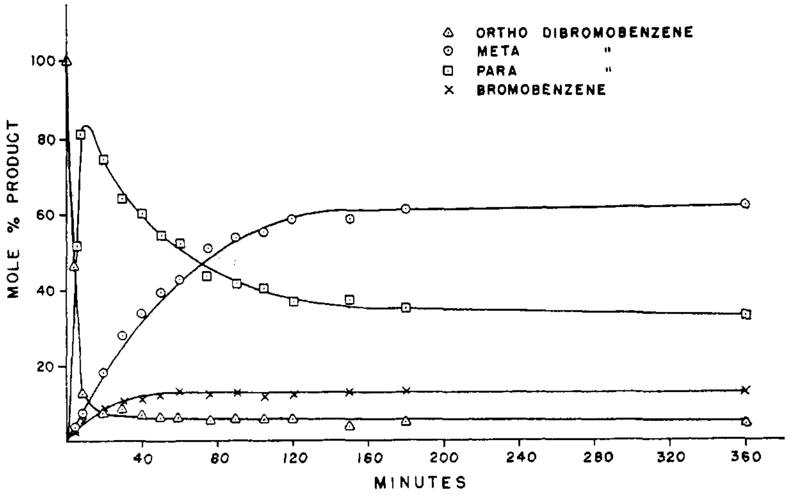
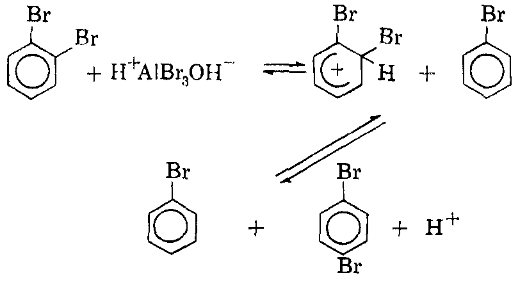


Fig. 9.—Isomerization of *o*-dibromobenzene with Al_2Br_6 at 30°.

usual way. Results of the experiment shown in Fig. 10 indicate a fast increase in the amount of dibromobenzene relative to those of the mono- and tribromobenzenes. The equilibrium values of the mono- and tribromobenzenes were reached in this case in the same time as in previous experiments where the starting reaction mixture contained none of these compounds.

Mechanism.—Concerning the mechanism of the aluminum bromide-catalyzed isomerization of bromofluorobenzenes, bromochlorobenzenes, and dibromobenzenes, a simple proton-catalyzed mechanism leading through a benzenonium type intermediate seems to be the most plausible. This mechanism in its initial step is identical with that proposed for the isomerization of the corresponding chlorofluorobenzenes and dichlorobenzenes[9] with the difference that the greater stability of a positively charged bromine species (in limiting case of the bromonium ion, Br^+) allows it more easily to be dispatched from the aromatic ring. This provides a possibility for intermolecular interactions as suggested for the fast *ortho-para* interchanges in the isomerization of *o*- and *p*-dibromobenzenes, bromochlorobenzenes, and bromofluorobenzenes.



In the intermolecular bromination step the halobenzene is brominated according to a pure electrophilic substitution reaction. In this kinetically controlled process the bromine atom may enter either the *ortho* or the *para* positions, showing directing effects similar to usual electrophilic aromatic bromination. Using heavy water-pretreated aluminum bromide as catalyst, with removal of deuterium bromide formed, this mechanism was directly substantiated through formation of ring-

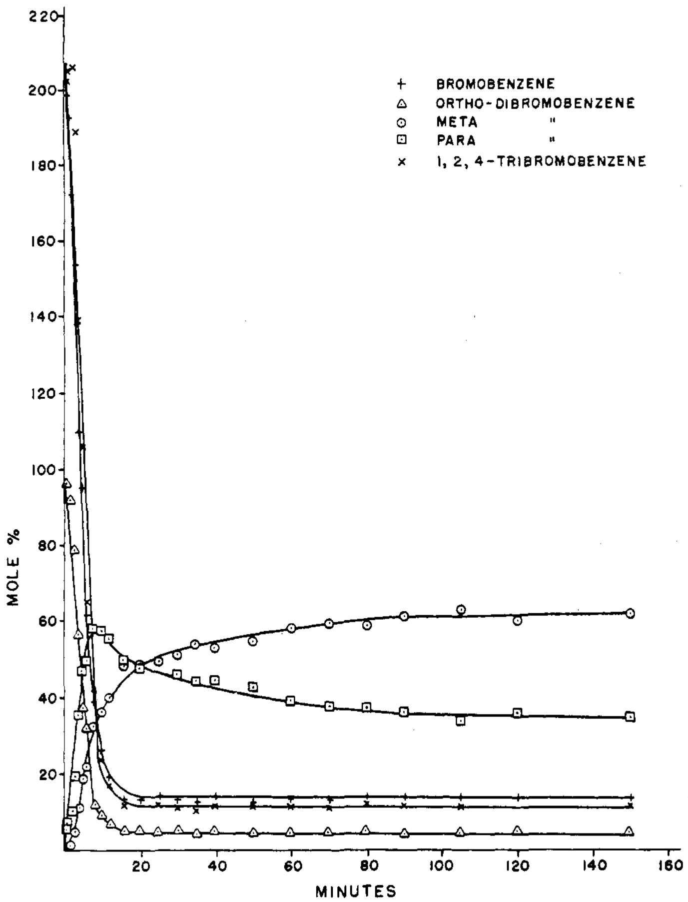
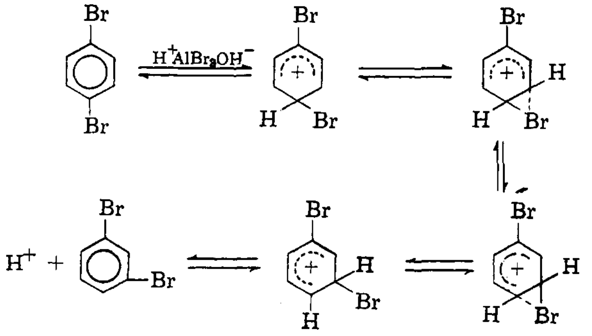


Fig. 10.—Isomerization of *o*-dibromobenzene in the presence of bromobenzene and 1,2,4-tribromobenzene with Al_2Br_6 + H_2O co-catalyst.

deuterated halobenzenes, similarly to that described previously in the investigation of the isomerization of dichlorobenzenes[9] and the disproportionation of halobenzenes.[7]

Concurrently with the fast intermolecular isomerization, however, slower intramolecular 1,2-shifts can also occur.



Thus a build-up of the *meta* isomer results, which itself, due to the fact that halogens in *meta* positions are not able to assist through conjugative stabilization sigma-complex formation, is not participating in intermolecular isomerization to a larger degree.

The slower 1,2-intramolecular shift mechanism suggested for the isomerization of *m*-dibromobenzene is identical in nature with that of the corresponding dichlorobenzene.

That the intermolecular isomerization of dibromobenzenes does not lead to a higher degree of disproportionation than observed, could be explained by the fact that after the detachment of the Br^+ ion there is a competition between the formed monohalobenzene and the present dihalobenzenes in the subsequent electrophilic bromination. The higher basicity of monohalobenzenes over the dihalobenzenes[8] (together with more favorable steric factors) allows preferentially the bromination of halobenzenes, thus causing the fast *ortho-para* interchange, over the formation of trihalobenzenes. The equilibrium

$$C_6H_5X + C_6H_3XBr_2 \underset{}{\overset{H^+AlBr_3OH^-}{\rightleftharpoons}} 2C_6H_4X\,Br$$

$$X = F, Cl, Br$$

was found to contain 13–15% trihalobenzenes, 12–13% halobenzenes (somewhat less than the equivdalent amount of trihalobenzene because of secondary reactions of monohalobenzenes), and about 72–75% dihalobenzenes.

Increased reaction temperatures leading to irreversible side reactions may further upset the stoichiometry of the equilibrium. *p*-Dibromobenzene isomerized at 180° for twelve hours yielded a mixture containing 26% tribromobenzene and only 7% monobromobenzene based on the amount of the remaining dibromobenzenes.

The time requirement of the *ortho* and *para* bromine atoms to reach the fast 1:6.5 quasi-equilibrium *ortho-para* ratio depends somewhat on the nature of the second substituent (and thus the basicity of the compounds) and increases in the order of Br < Cl < F, being about 2, 10, and 20 minutes, respectively, for dibromo-, bromochloro-, and bromofluorobenzene under the investigated experimental conditions at 30°.

Experimental

Materials.—Halobenzenes used were commercially available chemicals of highest purity, which were purified by fractional distillation on an Oldershaw column rated at 50 theoretical plates. Purity of these materials as determined by gas chromatography was 99.5% or higher. Aluminum bromide (Fisher reagent grade) was purified by vacuum sublimation.

Isomerization of Dihalobenzenes.—Aluminum bromide (0.05 mole) and 1 ml. of water were added to 0.5 mole of dihalobenzene in a flask equipped with magnetic stirrer and calcium chloride tube. The reaction mixture was kept in a thermostatically controlled bath with constant agitation. Samples of 1–2 ml. withdrawn at certain intervals were quenched with ice water, extracted with ether, and the organic layer was washed acid-free.

Gas-Liquid Chromatographic Analysis.—The ethereal solutions of the products after drying with calcium chloride were analyzed by gas-liquid chromatography using a Perkin-Elmer 154C Vapor Fractometer equipped with a Perkin-Elmer Model 194 electronic printing integrator. A four meter by 0.25-in. stainless steel column packed with polypropylene glycol (UCON LB-550-X) on diatomaceous earth was used, employing hydrogen (30 ml./min.) as carrier gas.

The relative response data of the materials investigated were obtained by analyzing synthetic mixtures of mono- and dihalobenzenes of known composition. An error of less than ±2 relative per cent was found for most constituents. The following retention times were observed for the halobenzenes analyzed.

RETENTION TIME OF HALO- AND DIHALOBENZENES

Compound	Column temperature	Retention time, min.
Benzene	145	2.5
Fluorobenzene	145	3
Chlorobenzene	180	4
Bromobenzene	180	6
o-Bromofluorobenzene	145	13
m-Bromofluorobenzene	145	11
p-Bromofluorobenzene	145	12
o-Bromochlorobenzene	180	16
m-Bromochlorobenzene	180	13
p-Bromochlorobenzene	180	14
o-Dibromobenzene	180	24
m-Dibromobenzene	180	21
p-Dibromobenzene	180	22

Friedel-Crafts Isomerization. IV.[1] Aluminum Halide-Catalyzed Isomerization of Halotoluenes

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The isomerization of fluorotoluenes, chlorotoluenes, and bromotoluenes has been investigated with water-promoted Al_2Cl_6. *m*- and *p*-fluorotoluene as well as the chlorotoluenes isomerize by an intramolecular 1,2-methyl shift mechanism. Due to the strongly deactivating influence of the fluoro substituent upon the *ortho* position, *o*-fluorotoluene undergoes halogen exchange with the catalyst and Friedel-Crafts type arylation reactions rather than isomerization. *m*-Bromotoluene isomerizes by an apparent 1,2-shift of the bromine while the isomerization of *o*- and *p*-bromotoluene involves an initial fast intermolecular bromine migration followed by a considerably slower rearrangement to the equilibrium mixture.

Many investigations of isomerization and disproportionation reactions of alkylbenzenes and halobenzenes under the influence of Lewis acids have been carried out. Less seems to be known of the behavior of substituted benzenes carrying both an alkyl and a halo substituent.

Norris and Turner[2] treated *o*-, *m*-, and *p*-chlorotoluene with aluminum chloride at temperatures up to 100° and found isomerization to occur readily, accompanied by some disproportionation. Cryoscopic and ebullioscopic methods were used to determine isomer distributions. An investigation of the aluminum halide-catalyzed isomerization of bromotoluenes over the temperature range −25 to 100° was carried out by Crump and Gornowicz.[3]

In the present study, fluorotoluenes, chlorotoluenes, and bromotoluenes were isomerized with water-promoted aluminum chloride using infrared analysis to establish isomer distributions. The change of isomer distribution with time allows some insight into the three-compound equilibrium and provides qualitative information regarding the relative velocity with which the individual isomers are formed.

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[1] Part III, *J. Org. Chem.*, **27**, 3455 (1962).

[2] J. F. Norris and H. S. Turner, *J. Am. Chem. Soc.*, **61**, 2128 (1939).

[3] J. W. Crump and G. A. Gornowicz, personal communication.