

Friedel-Crafts Isomerization. I. Effect of Promoted Aluminum Halides on Halobenzenes

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Disproportionation (intermolecular isomerization) of fluoro-, chloro-, and bromobenzene was investigated through the effect of water-promoted aluminum chloride and bromide. Investigations were carried out by the use of a gas-liquid chromatographic analytical method. It was observed that ring-bonded fluorine does not undergo intermolecular migration. The decreasing order of activity of halobenzenes in isomerization was found to be $\text{Br} \gg \text{Cl}$. The reaction mechanism of the intermolecular isomerization (disproportionation) of halobenzenes in terms of sigma complex type intermediate state formation is discussed as a consequence of the results obtained. The relative basicity of the halobenzenes determined from spectroscopic data is in agreement with this mechanism. Further proof of the suggested mechanism was obtained by using heavy water as the promoter. Halogen exchange and electrophilic arylations by the halobenzenes accompany the aluminum halide-induced isomerization of halobenzenes. In these reactions the relative order of activity of the halobenzenes was found to be $\text{F} > \text{Cl} > \text{Br}$. To explain the reversed order of activity as compared to that observed in isomerization and to account for the mechanism, intermediate complexing is suggested through the unshared pairs of the halogens to the acid catalyst (n-complex formation). Evidence for n-complexing of fluorobenzenes with aluminum bromide was obtained by infrared and high resolution nuclear magnetic resonance spectroscopy. Conductivity measurements were also in accordance with the proposed complex formation. Further proof of the n-complex mechanism was obtained by the chlorine exchange occurring between chlorobenzene and Al_2Cl_6 .⁶

Five years after Friedel and Crafts had first reported their findings on the action of aluminum chloride on organic chlorides, Dumreicher¹ found that bromobenzene was converted to benzene and dibromobenzene in the presence of aluminum bromide. A considerable amount of unchanged bromobenzene and some tarry material were also obtained. A year later Friedel and Crafts² themselves observed the transfer of chlorine during the methylation of *o*-dichlorobenzene, using methyl chloride in the presence of aluminum chloride. The principal products were hexamethylbenzene and trichloromesitylene. Simultaneously, an independent investigation of Leroy³ concerning the reaction of *p*-dibromobenzene with aluminum bromide, showed that, although the halogenated benzene was converted mainly into carbonaceous material, a mixture consisting of bromobenzene, *m*- and *p*-dibromobenzene, and two isomers of tri-bromobenzene was formed.

Halogen migration under Friedel-Crafts conditions in aromatic compounds was frequently investigated and a review of earlier work has been given by Thomas.⁴ It has been shown that aluminum chloride may catalyze the migration of a bromine atom from one aromatic nucleus to another. Thus, tribromophenol heated with benzene and aluminum chloride gives bromobenzene and phenol.⁵ Trichlorophenol fails to react under similar conditions, indicating that chlorine in the nucleus does not undergo migration as easily as bromine.⁶

Fairbrother^{7a} has measured the extent of the disproportionation of bromobenzene in the presence of aluminum bromide.

Although no quantitative determination of isomers was stated, Fairbrother found that "the isomer formed appears to be chiefly 1,4-dibromobenzene."

Vorozhtsov^{7b} found no isomerization when monofluoronaphthalenes were treated with aluminum chloride; however, some chloronaphthalenes were formed.

Besides the isomerizing effect of aluminum halides on halo- and dihalobenzenes, a limited amount of information is available on halogen exchange and arylation taking place under these conditions. The exchange of radioactive bromine between aluminum bromide and bromobenzene, is very slow at room temperature⁸ and slow even at 100°. It has been found that, whereas aluminum chloride has little effect on chlorobenzene,¹ the action of aluminum bromide on chlorobenzene yields bromobenzene.⁹ In relation to the arylating effect of halobenzenes under Friedel-Crafts conditions, it was found that bromobenzene reacts with naphthalene to give a 20% yield of phenylnaphthalene.¹⁰ Resorcinol reacts with 2-chloroquinoline to give a yield of 25% of dihydroxyphenylquinoline.¹¹

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Results

In order to obtain further information on the mechanism of aromatic isomerizations under Friedel-Crafts conditions, an investigation of the reaction of fluoro-, chloro-, and bromobenzene, was carried out with water-promoted aluminum chloride and aluminum bromide.

aluminum bromide and co-catalyst or with pre-treated aluminum bromide was kept at 0 or 30° and small samples of the mixture were withdrawn at certain intervals and quenched in ice water. In both cases the mixtures were washed acid-free, dried, and analyzed by gas-liquid chromatography. The results are summarized in Table I-X.

The use of water as co-catalyst eliminated the

TABLE I
EFFECT OF WATER-PROMOTED ALUMINUM CHLORIDE ON FLUOROBENZENE

Temp.	Time, days	C ₆ H ₆	C ₆ H ₅ F	C ₆ H ₅ Cl	C ₆ H ₄ ClF			C ₆ H ₄ Cl ₂		C ₆ H ₃ Cl ₂ F	
					<i>o</i> -, <i>m</i> -, <i>p</i> -	<i>o</i> -, <i>m</i> -, <i>p</i> -	C ₆ H ₄ F ₂	<i>o</i> -	<i>p</i> -		
85	1	0.0	100.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	
85 u.v.	1	.0	100.0	24.0	.0	.0	.0	.0	1.1	3.2	
150	14	Trace	100.0	32.4	Trace	Trace	.0	.0	1.8	5.3	
160	1	Trace	100.0	25.2	0.0	Trace	.0	.0	0.5	1.5	
240	1	Trace	100.0	41.1	Trace	0.9	.0	.0	.6	1.9	

Note: In Tables I to V the amount of each isomerization product is given as the molar percentage of the starting material.

TABLE II
EFFECT OF WATER-PROMOTED ALUMINUM BROMIDE ON FLUOROBENZENE

Temp.	Time, days	C ₆ H ₆	C ₆ H ₅ F	C ₆ H ₅ Br ^a	C ₆ H ₄ BrF			C ₆ H ₄ F ₂	C ₆ H ₃ Br ₂ F	
					<i>o</i> -	<i>m</i> -	<i>p</i> -		<i>o</i> -	<i>p</i> -
85	1	6.8	100.0	2.6	Trace	2.3	1.0	0.0	0.0	0.0
85 u.v.	1	6.9	100.0	6.1	0.7	4.7	1.7	.0	.0	.0
160	1	14.1	100.0	4.9	.6	2.0	0.8	.0	.0	.0
240	1	22.8	100.0	19.6	1.2	3.1	1.9	.0	.3	.8

^a High degree of disproportionation to benzene, dibromobenzenes, and higher boiling compounds always take place.

Though in the course of our investigations the obtained product mixtures were analyzed by a quantitative gas-liquid chromatographic method, the data obtained give only relative information on the isomerization processes. This is because a certain amount of tarry material of unknown composition was always formed in the aluminum halide-catalyzed isomerization of halobenzenes (and the subsequently investigated dihalobenzenes), the amount of which in certain cases was as high as 30% of the over-all material balance. All our data are related only to recovered analyzable material such as benzene, halobenzenes, dihalobenzenes, and diphenyls, neglecting the tarry materials of high molecular weight. The amounts of the isomerization products are given generally either as percentage of the amount of unchanged starting halobenzene or as a percentage of the sum of combined dihalobenzene isomers formed. In either case only relative amounts of products could be determined due to the varying amount of tarry by-products formed.

The following general procedure was used: In the case of fluorobenzene and chlorobenzene (which react very slowly) the organic material was mixed with aluminum halide and subsequently the co-catalyst (water or heavy water) was added to the mixture. The reaction mixture was refluxed or heated in an autoclave or in a sealed glass tube for periods of one day to three weeks.

Isomerization of bromobenzene being much faster than that of fluoro- or chlorobenzene proceeded fast even at 0°. Bromobenzene mixed with

TABLE III
ISOMERIZATION OF CHLOROBENZENE WITH WATER-PROMOTED ALUMINUM CHLORIDE

Temp.	Time, days	C ₆ H ₆	C ₆ H ₅ Cl	C ₆ H ₄ Cl ₂			C ₆ H ₃ Cl ₃ /C ₆ H ₅ Cl
				<i>o</i> -	<i>m</i> -	<i>p</i> -	
75	14	0.3	100.0	Trace	0.1	Trace	0.001
75	21	.4	100.0	Trace	.2	0.1	.003
132	1	.5	100.0	Trace	.2	.1	.003
200	2	.3	100.0	Trace	.6	.2	.008
200	14	1.7	100.0	0.3	2.4	1.6	.043

necessity of maintaining the systems under rigidly anhydrous conditions. It was also observed that water as a co-catalyst had a strong effect on the reactions. Already Fairbrother and Scott⁷ reported that the disproportionation of bromobenzene by Al₂Br₆ is slow in dilute solutions but traces of hydrogen bromide are co-catalysts for the reaction. In our experiments, bromobenzene reacted fast at 30° in the presence of water-promoted Al₂Br₆, giving the dibromobenzene isomerization equilibrium mixture in ten minutes. When the reaction was carried out with carefully dried reagents in the absence of moisture forty minutes was needed to reach the equilibrium. At 0° the reaction time needed to reach equilibrium was more than six hours. It is obvious that by the improvement of the experimental techniques to achieve even drier reaction conditions, the reaction times could be expected to increase even further. The reaction may proceed, however, even in the most carefully dried system, as there is the possibility of ring halogenation or condensations by aluminum halides, both re-

TABLE IV
 ISOMERIZATION OF CHLOROBENZENE WITH WATER-PROMOTED ALUMINUM BROMIDE

Temp.	Time, days	C ₆ H ₆	C ₆ H ₅ Cl	C ₆ H ₅ Br	C ₆ H ₄ Cl ₂			C ₆ H ₄ ClBr			C ₆ H ₄ C ₆ H ₄ Cl	C ₆ H ₄ Cl ₂ /C ₆ H ₅ Cl
					<i>o</i> -	<i>m</i> -	<i>p</i> -	<i>o</i> -	<i>m</i> -	<i>p</i> -		
85	1	0.25	100.0	Trace	0.0	0.0	0.0	Trace	0.3	0.2	0.0	0.0
132	1	.5	100.0	0.1	Trace	Trace	Trace	Trace	.3	.2	.0	.0
132 u.v.	1	.8	100.0	.2	Trace	Trace	Trace	Trace	.4	Trace	.0	.0
240	1	6.3	100.0	18.6	0.5	9.7	0.9	0.2	.9	0.5	.9	.11

 TABLE V
 ISOMERIZATION OF BROMOBENZENE WITH WATER-PROMOTED ALUMINUM CHLORIDE

Temp.	Time, days	C ₆ H ₆	C ₆ H ₅ Cl	C ₆ H ₅ Br	C ₆ H ₄ Cl ₂	C ₆ H ₄ Br ₂		
						<i>o</i> -	<i>m</i> -	<i>p</i> -
85	1	16.0	Trace	100.0	0.0	0.6	8.9	3.4
156	1	30.7	1.7	100.0	.8	1.0	7.9	2.9
156 u.v.	1	30.1	1.5	100.0	.4	1.1	8.4	3.2

TABLE VI

ISOMERIZATION OF BROMOBENZENE WITH WATER-PROMOTED ALUMINUM BROMIDE AT 30°

Time, min.	C ₆ H ₆	C ₆ H ₅ Br	C ₆ H ₄ Br ₂			C ₆ H ₄ Br ₂ /C ₆ H ₅ Br
			<i>o</i> -	<i>m</i> -	<i>p</i> -	
0.0	0.0		0.0	0.0	0.0	0.0
.5	87.2	6750	12.1	.8	87.1	.01
1.0	85.4	3020	9.3	10.3	80.4	.03
1.5	75.9	1370	10.2	17.8	72.0	.07
2.0	74.1	738	8.7	27.5	63.8	.13
2.5	77.8	543	7.5	33.0	59.5	.18
3.0	73.4	412	6.1	44.3	49.6	.24
4.0	71.5	295	5.6	52.9	41.5	.33
5.0	71.2	221	4.8	61.4	33.8	.45
10.0	71.0	187	4.3	62.5	33.2	.53

Note: In Tables VI to X the amount of each isomerization product is given as the molar percentage of the sum of the three dibromobenzene isomers formed during the reaction.

TABLE VII

ISOMERIZATION OF BROMOBENZENE WITH ALUMINUM BROMIDE AT 30°

Time, min.	C ₆ H ₆	C ₆ H ₅ Br	C ₆ H ₄ Br ₂			C ₆ H ₄ Br ₂ /C ₆ H ₅ Br
			<i>o</i> -	<i>m</i> -	<i>p</i> -	
0	0.0		0.0	0.0	0	0.00
1	100.0	25000	Trace	.0	Trace	.00
3	73.9	4350	14.6	Trace	85.4	.02
5	80.2	893	15.9	2.0	82.1	.11
7	75.1	726	14.3	4.8	80.9	.14
10	76.4	614	11.6	11.3	77.1	.16
15	77.8	560	9.0	27.4	63.6	.18
20	75.0	439	6.7	45.6	47.7	.23
25	73.6	375	5.5	53.9	40.6	.26
30	70.9	340	5.7	60.1	34.2	.29
40	74.2	294	5.0	63.7	31.3	.34
50	67.5	313	4.6	62.4	33.0	.32
60	72.2	261	4.5	62.8	32.7	.38
90	70.3	263	4.7	61.9	33.4	.38

actions leading to the formation of hydrogen halide which is known to co-catalyze isomerization.^{7a}

Discussion

The experimental results obtained indicate clearly that the halobenzenes investigated undergo three different types of reactions in the presence of promoted aluminum halides: (1) isomerization, (2) halogen exchange, and (3) Friedel-Crafts arylation. Consequently, the results and their in-

TABLE VIII

ISOMERIZATION OF BROMOBENZENE WITH ALUMINUM BROMIDE AT 0°

Time, min.	C ₆ H ₆	C ₆ H ₅ Br	C ₆ H ₄ Br ₂			C ₆ H ₄ Br ₂ /C ₆ H ₅ Br
			<i>o</i> -	<i>m</i> -	<i>p</i> -	
3	80	10,000	14.0	0	86.0	0.0100
4	80	6,200	14.9	0	85.1	.0161
5	76.9	2,860	14.3	0	85.7	.0349
6	78.3	2,470	14.6	0	85.4	.0404
8	81.2	1,540	15.1	0	84.9	.0649
10	78.7	1,110	14.5	Trace	85.5	.0900
12	77.1	996	14.2	Trace	85.8	.100
16	83.4	785	14.8	1.8	83.4	.127
20	75.8	732	11.1	5.6	83.3	.137
25	72.6	698	11.9	6.1	82.0	.143
30	74.5	637	11.7	7.6	80.7	.157
35	79.3	610	9.8	10.3	79.9	.164
40	76.7	605	10.2	11.2	78.6	.165
50	80.1	528	8.4	16.5	75.1	.189
60	77.0	545	8.5	20.8	70.7	.183
70	77.9	504	7.7	24.1	68.2	.198
80	72.4	502	7.2	23.9	68.9	.199
90	73.5	507	4.9	28.0	67.1	.197
105	76.2	483	6.2	30.2	63.6	.207
120	75.7	510	5.6	36.5	57.9	.196
150	74.6	469	6.0	45.3	48.7	.213
180	77.6	444	6.5	51.5	42.0	.225
360	69.3	418	4.6	60.6	34.8	.239
1 week	65.8	329	4.3	62.2	33.5	.304

TABLE IX

ISOMERIZATION OF BROMOBENZENE WITH ALUMINUM BROMIDE AT 25° CATALYST MOLE FRACTION 0.005

Time, hr.	C ₆ H ₆	C ₆ H ₅ Br	C ₆ H ₄ Br ₂			C ₆ H ₄ Br ₂ /C ₆ H ₅ Br
			<i>o</i> -	<i>m</i> -	<i>p</i> -	
0.5	93.7	6750	14.4	0.0	85.6	0.01
1	92.3	1970	14.8	Trace	85.2	.05
2	83.2	880	12.9	3.1	84.0	.11
3	85.6	648	12.0	4.3	83.7	.15
6	68.5	524	10.8	11.5	77.7	.19
72	67.4	488	7.7	28.1	64.2	.21
96	65.9	465	7.9	28.7	63.4	.22
168	50.6	425	7.0	30.1	62.9	.24

terpretation are being treated separately for each of these reactions.

Isomerization.—It was found that ring-bonded fluorine did not take part in migration with Al₂Cl₆ or Al₂Br₆. In the case of fluorobenzene, no trace of difluorobenzene formed at 150° after fourteen days or even at 240°. On the other hand, bromobenzene isomerizes easily. Chlorobenzene shows a lower,

TABLE X
ISOMERIZATION OF BROMOBENZENE WITH ALUMINUM
BROMIDE AT 25° CATALYST MOLE FRACTION 0.002

Time, hr.	C ₆ H ₆		C ₆ H ₅ Br ₂			C ₆ H ₅ Br ₂ / C ₆ H ₅ Br
	C ₆ H ₆	C ₆ H ₅ Br	<i>o</i> -	<i>m</i> -	<i>p</i> -	
0.5	90.1	5765	15.1	0.0	84.9	0.02
1.0	87.4	2503	16.3	.0	83.7	.04
2.0	84.8	2308	14.1	Trace	85.9	.04
3.0	84.6	1709	15.4	0.8	83.8	.06
6.0	79.5	1556	16.0	1.0	83.0	.06
24.0	68.2	1413	15.0	0.9	84.1	.07
72.0	65.7	1367	13.8	1.0	85.2	.07
168.0	57.0	1105	13.9	1.3	84.8	.09

but still noticeable reactivity. As seen from data of Tables III–VIII, chlorobenzene disproportionates with promoted aluminum chloride at 200° after fourteen days to about 4.3%. With aluminum bromide at 240° 11.3% disproportionation was obtained. In contrast, bromobenzene with promoted aluminum bromide at 30° gave 53.5% disproportionation after ten minutes. Without promoter under identical conditions 16.3% isomerization was observed at 30° and only 9% at 0° after ten minutes. The order of reactivity of halogens in the isomerizations effected by aluminum halides is, therefore, Br ≫ Cl. This is in accordance with the relative stability of positively polarized halogen entities or in limiting case the halonium ions Br⁺ > Cl⁺. The failure of ring-bonded fluorine to undergo isomerization can best be interpreted on the basis that fluorine is unable to form a cation or any positively polarized entity.

Although a large number of data are available on the basicity of alkylbenzenes, considerably less data have been published on the basicity of halobenzenes.

Attempts were made to correlate the strengths of donor-acceptors complexes with the ionization potentials of the donors¹² and infrared stretching frequencies of acids in halobenzenes.^{13,14}

Based on available data,¹⁴ the relative order of basicity of halobenzenes and that of benzene is

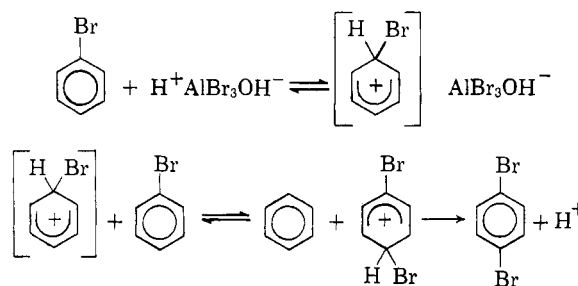


This is in agreement with the generally accepted fact that in halobenzenes the negative inductive effect of the halogen is larger than the opposed conjugative effect; $-I > +T$.

There are, however, no reliable data on the relative strengths of the opposed inductive and conjugative effects.

In accordance with the relative basicity of the halobenzenes, it is to be expected that bromobenzene will possess a higher degree of activity than chlorobenzene (or fluorobenzene) in a mechanism involving protonation of the ring to a sigma complex and subsequent positively polarized halogen

elimination from the sigma complex by nucleophilic replacement by a second molecule of halobenzene.



As can be seen in Table VI–VIII the formation of dibromobenzene in the disproportionation reaction follows a practically pure electrophilic bromobenzene bromination pattern at first with about 85% *p*- and 15% *o*-dibromobenzene isomers found and no trace of *m*-dibromobenzene present.¹⁵ This intermolecular reaction is kinetically controlled while the formation of *m*-dibromobenzene, starts only after a longer period of time (five minutes at 30° and fifteen minutes at 0° in the absence of co-catalyst) and increases slowly to the equilibrium concentration of 62%.¹⁶ This second intramolecular stage of the isomerization is thermodynamically controlled.

The kinetically controlled fast intermolecular isomerization step can be separated from the thermodynamically controlled intramolecular isomerization even better if the action of aluminum bromide on bromobenzene is investigated with very low catalyst concentrations, similarly to the work of Fairbrother.⁷ Data of quantitative determination of the amount of benzene and dibromobenzenes formed, together with the determination of the isomer ratios, are summarized in Tables IX and X. The *para-ortho* directing effect of bromine is obvious in the dibromobenzenes formed. Although some isomerization occurred under the experimental conditions (as shown in the increasing amount of *meta* isomer formed with time), it has not approximated the thermodynamic equilibrium obtained when higher catalyst concentrations were used.

If the intermolecular isomerization proceeded according to a mechanism not involving any positive halogen species, fluorobenzene might be expected to isomerize as well. The differences in the basicity of the various halobenzenes alone are not large enough to warrant any qualitative differences among the halobenzenes. The σ -complex mechanism, however, represents only the limiting structure for the reaction path. The primary interaction of the acid catalyst and the halobenzene involves only a weaker interaction at first in the form of an oriented π -complex (or outer complex). This more

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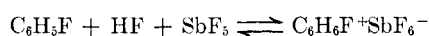
(13) M. L. Josien and G. Sourisseau, "Hydrogen Bonding," Ed. D. Hadzi, Pergamon Press, New York, N. Y., 1959, p. 135.

(14) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4581 (1961).

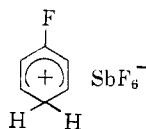
(15) Electrophilic bromination of halobenzenes with what is believed a positive bromine species is being reported in a forthcoming paper of our investigations on aromatic substitution.

(16) For the equilibrium data of dibromobenzenes see subsequent paper, *J. Org. Chem.*, **27**, 3455 (1962).

labile intermediate then passes to the σ -complex stage somewhere during the reaction path. The elimination of the halonium ion again proceeds through an oriented π -complex (or outer complex). Unlike the case of alkylbenzenes there has been no direct proof until now for the existence of σ -complexes of halobenzenes. Owing to the low basicity of the halobenzenes as compared with that of the alkylbenzenes, isolation of intermediate σ -complexes is not generally possible, as interaction between the acid catalyst and the halobenzene does not occur at low temperatures suitable for complex isolations.¹⁷ Recently, however, a stable benzenonium ion (σ -complex) was isolated from fluorobenzene, hydrogen fluoride, and antimony pentafluoride,¹⁸



N.m.r. investigation in sulfur dioxide solution has shown that protonation takes place preferentially in the *para* position. Thus the benzenonium complex is stabilized by the conjugative effect of the fluorine atom affecting the *para* position.



We suppose that the stability of the $\text{C}_6\text{H}_6\text{F}^+\text{SbF}_6^-$ complex is due mainly to the stabilizing effect of conjugation by the unshared electron pairs of fluorine in the *para* position. Consequently it does not mean a higher π -basicity for fluorobenzene itself, only an increased stabilization of the once-formed complex. As from previous data fluorobenzene seems to be the least basic among the halobenzenes, this result could be interpreted as proof for the fact that halobenzenes, similarly to alkylbenzenes, can be protonated by suitable strong acids to σ -complex type intermediates, even if the isolation of these proves to be difficult due to the lack of sufficiently strong conjugative effects.

In order to obtain further evidence for the suggested σ -complex mechanism involving primary ring protonation with subsequent halonium ion elimination, heavy water was used as a promoter in some experiments.

A vacuum technique similar to that used by Pines¹⁹ in the case of the isomerization of *n*-butane was employed in our study of the effect of heavy water upon the isomerization of halobenzenes.

The following two methods were used: (1) Aluminum chloride or bromide was treated with varying amounts of heavy water. The mixtures

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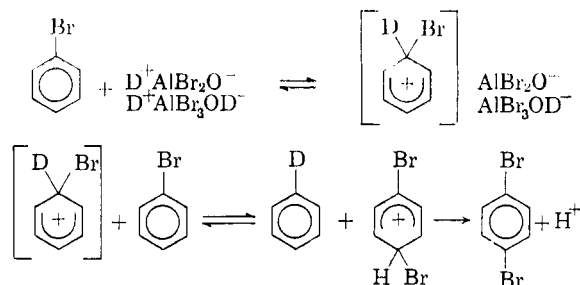
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were heated in vacuum and the liberated deuterium halide was pumped off. The resulting pretreated catalyst, freed of uncombined deuterium halide, was then used in the isomerization of halobenzenes. (2) Aluminum halide, halobenzene, and heavy water were mixed without previous removal of deuterium halide.

Pretreated catalysts, with complete removal of liberated deuterium halide, gave results similar to the experiments in which heavy water was added to the halobenzene-aluminum halide mixture without the removal of deuterium halide. Pretreated aluminum bromide was generally more active than pretreated aluminum chloride.

Concerning the nature of the pretreated catalysts, it is difficult to express any final opinion at present. Pines¹⁹ suggested AlBr_2OD as structure for the heavy water pretreated aluminum bromide catalyst. Although our analytical data are in accordance with the composition of AlX_2OD ($\text{X} = \text{Cl}, \text{Br}$) and infrared spectra point to the presence of O—D bands, there is no evidence that a uniform compound was obtained.

Bromobenzene was treated with deuterium oxide-promoted aluminum bromide and with pretreated catalyst obtained by pumping off any deuterium bromide formed by the interaction of aluminum bromide with deuterium oxide. The isomerization products from both reactions (benzene, dibromobenzenes, and unchanged bromobenzene) were analyzed by spectroscopic methods. It was found that the benzene formed contained a considerable amount of *d*-benzene (as proved by the C—D stretching frequency in the infrared spectrum and mass spectroscopy). The recovered bromobenzene also contained ring deuteration but only in small amounts. The dibromobenzenes formed were practically free from ring deuteration. Consequently, to account for this finding, a primary ring deuteration involving a sigma-complex type intermediate seems to be most probable.



Halogen Exchange.—As may be observed from the experimental data, aluminum chloride and bromide have a marked effect on halobenzenes besides that of isomerization, *viz.*, a marked halogen exchange and electrophilic arylation giving halodiphenyls. It was observed that fluorobenzene is considerably more reactive in halogen exchange with aluminum halides than either chloro- or bromo-

benzene. In order to be able to compare the relative reactivity of halobenzenes with aluminum halides in the halogen exchange reaction, the reaction of fluoro-, chloro-, and bromobenzene with aluminum chloride was investigated under identical reaction conditions. In the case of fluorobenzene and bromobenzene the degree of exchange reaction was easily followed by analyzing the formed chlorobenzene. In the case of chlorobenzene it was necessary to use Cl^{36} -labeled aluminum chloride in order to be able to determine the extent of halogen exchange. Treating the halobenzenes with water-promoted aluminum chloride in sealed tubes at 160° for twenty-four hours and analyzing the degree of halogen exchange by the amount of chlorobenzene formed from fluorobenzene and bromobenzene by gas-liquid chromatography, or in the case of chlorobenzene by determining the percentage of radioactive Cl^{36} introduced into chlorobenzene by the exchange reaction, the following percentages of exchange were obtained.

Halobenzene	% exchange
Fluorobenzene	25.2
Chlorobenzene	7.8
Bromobenzene	1.7

Thus the decreasing order of reactivity of halobenzenes in the halogen exchange reaction with aluminum chloride is $\text{F} > \text{Cl} > \text{Br}$.

A similar exchange reaction takes place with aluminum bromide, but due to the strong disproportionation of the bromobenzene formed with the catalyst at the necessary reaction temperatures, no quantitative evaluation of the data is possible. However, it was quite obvious from the experimental data that fluorobenzene exchanges much faster than chlorobenzene. The exchange reaction of bromobenzene with Br^{82} aluminum bromide was investigated earlier by Fairbrother⁸ who found it fairly slow even at 100° . Thus an identical relative order of reactivity of halobenzenes is also valid for the aluminum bromide exchange reaction.

To explain the reverse order of activity of halobenzenes in the exchange reaction and to account for the exchange reaction itself, a mechanism involving the complexing of the aluminum halide through the unshared pair of ring halogens (*n*-complexing) must be considered.

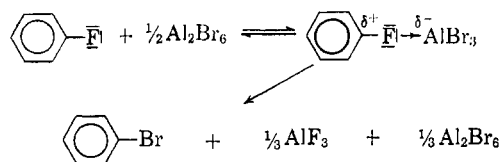
The term *n*- (or onium) donor base was introduced by Mulliken.^{18,20} Consequently, it is suggested that the term "n-complexes" be used to designate intermediates formed by the complexing of halogen atoms in halobenzenes (*n*-bases) with the acceptors (being the vacant orbital acceptors of the AlX_3 type in our case), in order to differentiate from π - and σ -complexing involving the π -electron system of the aromatic ring as donor center.

Aromatic hydrocarbons, as well as unsaturated aliphatics, are among the best known types of π -

bases. Halobenzenes have the ability to act both as π - or *n*-bases. This was demonstrated in the case of halogens which can combine either with π - or *n*-bases.²¹ Hydrogen halides, although they are strong acids in the Bronsted sense, act as weak Lewis acids somewhat like halogens in many cases. The Lewis acid character of halogens and hydrogen halides is attributed to the incompletely satisfied electronegativity of the halogen atoms. Since the acquisition of a negative charge by a halogen can take place only concurrently with a pronounced loosening of a covalent binding, these and similar Lewis acids, *e.g.* alkyl halides, are designated by Mulliken^{18,20} as *d*-acids (dissociate acids).

The unshared electron pairs of halogens can act as *n*-donors themselves in the presence of a sufficiently strong acceptor acid.

In interpretation of the mechanism of the halogen exchange reaction of fluorobenzene with aluminum bromide, this results in the loosening of the aromatic carbon-halogen bond. The negatively polarized halogen is then extracted by the strong acid (*e.g.* aluminum bromide or $\text{H}^+\text{AlBr}_4^-$ in our experiments). The aluminum-fluorine bond calculated from available thermochemical data is considerably stronger than the corresponding aluminum-chlorine or aluminum-bromine bond. Bond energies in kcal./mole, are: $\text{Al}-\text{F}$ 110.0, $\text{Al}-\text{Cl}$ 90.5, $\text{Al}-\text{Br}$ 78.0, and $\text{Al}-\text{I}$ 65.5. This helps to overcome the larger bond dissociation energy of the $\text{C}-\text{F}$ bond in fluorobenzene. The C-halogen bond dissociation energies in the halobenzenes according to Smith²² are the following (in kcal./mole) $\text{C}_6\text{H}_5-\text{F}$ 115, $\text{C}_6\text{H}_5-\text{Cl}$ 86, $\text{C}_6\text{H}_5-\text{Br}$ 71, $\text{C}_6\text{H}_5-\text{I}$ 57. Fluorine will thus be retained by the aluminum and the intermediate complex decomposes with halogen exchange taking place with simultaneous formation of aluminum fluoride. The mechanism could be accordingly written in terms of an *n*-complex intermediate as follows:



Evidence for the suggested *n*-complex mechanism was obtained from the infrared and high resolution nuclear magnetic proton and fluorine resonance spectroscopic investigation of the fluorobenzene-aluminum bromide complex.

The main carbon-fluorine infrared stretching absorption in fluorobenzene is at 1217 cm.^{-1} (vs). In the fluorobenzene: aluminum bromide complex

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(50% solution of aluminum bromide in fluorobenzene), the C—F stretching frequency is shifted to 1192 cm.^{-1} (s). The shift of 25 cm.^{-1} is attributed to n-complexing of the C—F bond ($\text{C}_6\text{H}_5\text{F}$) \rightarrow AlBr_3). The intensity of the shifted band was found to be dependent on the concentration of the complex in the fluorobenzene solution. The spectra were obtained on a Perkin-Elmer Model 221-G double beam grating spectrophotometer equipped with sodium chloride optics.

The high resolution fluorine magnetic resonance spectrum of the fluorobenzene: aluminum bromide complex (obtained on the modified n.m.r. spectrograph of Baker²³ at 56.457 Mc., using trifluoroacetic acid as external reference) shows the disappearance of the original many line spectrum²⁴ of fluorobenzene and the appearance of a broad line (about 25 c.p.s., not as broad as the original fluorobenzene spectrum) with considerably lower shielding. The observed shifts to lower shielding were for a 12% solution, 37 c.p.s.; for a 25% solution, 58 c.p.s.; and for a 50% solution, 91 c.p.s. The shift to lower shielding indicates electron donation by the fluorine atom. The proton resonance (obtained at 60.008 Mc., using water as external reference) of the many line fluorobenzene spectrum changes in the fluorobenzene: aluminum bromide complex (12.5% solution in fluorobenzene) into a broad peak (100 c.p.s. wide), with a marked shift (~ 40 c.p.s.), to a higher shielding, which could not be in accordance with the ring π -electron system acting as donor in the complex formation.

Conductivity measurements of solutions of Al_2Br_6 in fluorobenzene were carried out under exclusion of moisture. Purified fluorobenzene with a specific conductivity of 4.5×10^{-8} mho/cm. and three times resublimed aluminum bromide were used. All materials were handled under vacuum conditions, the solutions being made up by dilution technique. The equivalent conductivity of the solutions was found to vary linearly with the concentration of Al_2Br_6 in fluorobenzene as illustrated in Fig. 1.

Although it is difficult to come to a conclusion from conductivity data obtained in organic solvents, the linear correlation of the equivalent conductivity with the Al_2Br_6 concentration in fluorobenzene seems to be in accordance with the suggested n-complex formation giving rise to a conducting, highly polarized entity. Aluminum bromide, should it be dissolved without complex formation, or should it be only π -complexed by the ring itself, could hardly explain the observed conductivity data. Solutions of Al_2Br_6 in benzene have practically no conductivity.²⁵ The specific conductivity of a 20% Al_2Br_6 solution in benzene (specific conductivity = 1×10^{-13} mhos/cm.) was

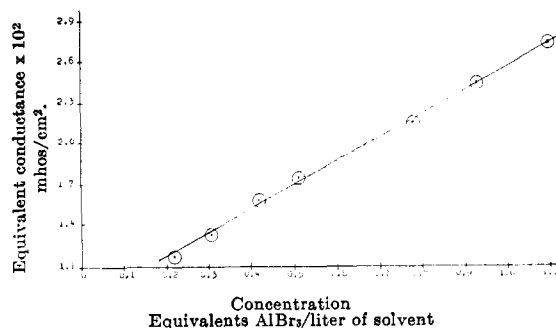


Fig. 1.—Conductivity of the $\text{C}_6\text{H}_5\text{F}:\text{AlBr}_3$ system.

found by Wertyporoch²⁶ to be lower than 3×10^{-9} mhos/cm. For a similar 20% Al_2Br_6 solution in fluorobenzene, the specific conductivity was found to be 2.26×10^{-5} mhos/cm. π -Complexing of Al_2Br_6 must be stronger in benzene, which is considerably more basic, than in fluorobenzene. The values obtained can be explained in accordance with the suggested n-complex formation, which accounts for a much stronger complex formation with fluorobenzene.

The marked effect of ultraviolet irradiation observed on the halogen exchange reaction is in accordance with previous observations²⁷ on metal fluorides and with observations on the effect of ultraviolet irradiation in different Friedel-Crafts reactions. In the ultraviolet irradiation of fluorobenzene with aluminum bromide at 85° , for example, the results obtained were almost identical with those carried out without irradiation at 160° . Thus, it seems possible to furnish a part of the necessary activation energy by means of irradiation instead of heat even in an obviously ionic reaction. Probably the effect is not so much that of loosening the C-halogen bond (the ultraviolet absorption of which is low) but effecting dissociation of the aluminum halide dimer, and thus facilitating the formation of the monomeric AlX_3 needed for the n-complex formation. This, of course, also explains why the aluminum bromide reactions were so much more affected by ultraviolet light than the aluminum chloride ones.

It is also interesting to note that in experiments using boron tribromide, which is monomeric, ultraviolet irradiation had no effect.

The presence of chlorofluorobenzene and bromofluorobenzene isomers obtained by the interaction of Al_2Cl_6 or Al_2Br_6 on fluorobenzene (as shown in Tables I and II), can be easily explained by the fact, that as a consequence of halogen exchange chloro- and bromobenzene are formed in the system. During disproportionation of these in the reaction mixture, the formed positive halogen ion is trapped by excess fluorobenzene.

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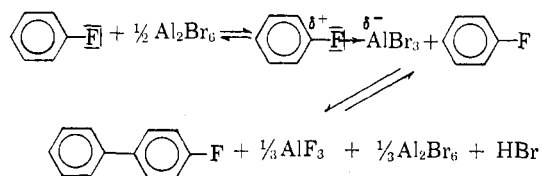
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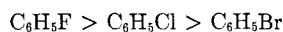
(27) G. A. Olah and A. Pavlath, *Acta Chim. Acad. Sci. Hung.*, **3**, 191 (1953); G. A. Olah, A. Pavlath, and G. Hosszang, *ibid.*, **8**, 41 (1956).

Friedel-Crafts Arylation.²⁸—When the reaction of aluminum chloride and bromide with fluorobenzene was investigated at 160 and 240°, as well as under the effect of ultraviolet radiation, a small amount of fluorobiphenyl (less than 10%) was always obtained (Tables I and II). On analysis by gas chromatography, it was found to have a composition of 75.2% 4-fluorobiphenyl and 24.8% 2-fluorobiphenyl with no trace of the 3-isomer being present. This proves that an electrophilic type of arylation of the fluorobenzene takes place, because in a radical type of reaction, a substantial amount of the meta isomer should also be formed.²⁹ In order to account for the electrophilic Friedel-Crafts type arylation, a mechanism similar to that of Brown³⁰ for the electrophilic Friedel-Crafts alkylation with primary alkyl halides is suggested.

Fluorobenzene and aluminum bromide form an n-complex (similar in nature to the primary alkyl halide-Lewis acid complex) and a second molecule of fluorobenzene (or other aromatic) displaces the complex in a concerted termolecular step.



Results similar to these but with considerably lower yields (less than 1%), were obtained with chlorobenzene at 240°. No biphenyl formation was observed at lower temperatures. In the case of bromobenzene, no bromobiphenyls were detected, although the higher molecular weight residues obviously contain products formed by similar arylation. Easy disproportionation of bromo aromatic compounds may be the cause of difficulty in observing the formation of bromobiphenyls. The relative order of activity of the halobenzenes in electrophilic arylation is, thus,



which is similar to the order observed in the alkylation activity of alkyl halides in Friedel-Crafts reactions.³¹

Experimental

Materials.—The halobenzenes used were commercially available chemicals of highest purity, which were purified by fractional distillation on an Aldershaw column rated at 50 theoretical plates. Purity of these materials as determined

by gas chromatography was 99.5% or higher. Aluminum chloride and bromide were Fisher reagent grade materials purified by repeated vacuum sublimation.

Al_2Cl_6 ³⁶ was obtained from the Volk Radiochemical Co., Chicago, Illinois.

Reactions of Halobenzenes with Aluminum Halides. (1) **Fluoro- and Chlorobenzene.**—Aluminum halide (0.05 mole) was added to 0.5 mole of halobenzene which had been weighed into a round-bottomed flask. Water (0.05 mole) was then added and the mixture was refluxed or heated for a period of 24 hr. at the given temperature. After cooling, the reaction mixture was poured on crushed ice. The quenched product was filtered, washed with water to remove last traces of acid, and the organic layer was separated. After drying over calcium chloride, the products were analyzed by gas chromatography.

High temperature, superatmospheric experiments were carried out either in sealed Pyrex glass tubes heated in an oven or in a glass-lined autoclave (1.5 in. i.d. \times 20-in. long). The autoclave was kept at the appropriate temperature with continuous efficient shaking of the contents. At the end of that time, the reaction mixture was worked up as before.

Experiments involving ultraviolet radiation of the reactions by means of a 700-w. Hanovia lamp, were carried out in quartz apparatus. Irradiation was continued for 24 hr. followed by working up of the mixtures as before.

(2) **Bromobenzene.**—Aluminum halide (0.5 mole) was added to 0.5 mole of bromobenzene and 0.05 mole of water in a flask which was equipped with a magnetic stirrer and was kept in a constant temperature bath. Samples of 1–2 ml. were withdrawn from the constantly stirred mixture in certain intervals and quenched with ice water. The samples after dilution with ether were worked up as before.

Exchange of Chlorobenzene with Al_2Cl_6 .³⁶—Chlorobenzene was treated with aluminum chloride, containing a known amount of Cl^{36} tracer under the same conditions as described previously. Reactions were carried out in sealed glass tubes at 160° for 24 hr. The reaction mixture was quenched with water, the organic (chlorobenzene) layer was extracted with toluene and washed acid-free with water. The collected washing water and organic layer was handled carefully to avoid losses. Radioactivity of the washing water (containing Cl^{36} from unchanged Al_2Cl_6 ³⁶) and organic layer (toluene solution of isomerization and exchange products of chlorobenzene containing Cl^{36} from halogen exchange) was analyzed for radioactivity using liquid scintillation radioassay with TriCarb L.S. spectrometer. Toluene scintillator solutions were used for the organic layer (toluene solution of chlorobenzene³⁶), and the data were extrapolated to zero concentration to compensate for quenching. Toluene/alcohol scintillator was used for the water washes. Packard sealed standard of Cl^{36} was used to standardize procedure for the toluene solution. Radiochlorine found in the toluene layer (from chlorobenzene- Cl^{36}) was expressed as percentage of unchanged radiochlorine from the aqueous layer.

Analysis.—The dried products were analyzed by gas-liquid chromatography using a Perkin-Elmer 154C Vapor Fractometer. The instrument was fitted with a stainless steel column (4 m. \times 1/4 in.) containing polypropylene glycol (UCON LB-550-X) supported on diatomaceous earth and operated generally at 195°, although temperatures as low as 80° were required for the resolution of benzene, fluorobenzene and difluorobenzene isomers. Hydrogen (or helium) flowing at 60 cc./min. was utilized as carrier gas. Samples (100 $\mu\text{l.}$) were injected.

From the areas of individual peaks, mole % figures were calculated for each product after determining relative response data following the method of Messner, Rosie, and Argabright.³² The method was calibrated using known mixtures and the error present in these analyses was found to be smaller than 3 relative per cent.

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Individual peaks were identified by the retention times of pure halobenzenes and dihalobenzene isomers. Identification of separated fractions in a number of preparative scale runs was made by infrared spectroscopy. Components were separated from the reaction mixture using a 3 m. \times 1 in. aluminum preparative-scale column packed with polypropylene glycol supported on diatomaceous earth. Samples of up to 5 ml. were separated by this method.

Acknowledgment.—The authors are indebted to Dr. E. B. Baker for the n.m.r. and to Dr. D. Cook for the infrared investigations, to Dr. F. A. Blanchard for radioactive analyses, to Dr. D. N. Glew for the calculation of bond energies, and to Dr. H. W. Quinn for conductivity measurements.

Friedel-Crafts Isomerization. II.¹ Aluminum Chloride-Catalyzed Isomerization of Chlorofluorobenzenes and Dichlorobenzenes. The Effect of Aluminum Chloride on Difluorobenzenes

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The water-promoted, aluminum chloride-catalyzed isomerization of chlorofluorobenzenes takes place by an intramolecular 1,2-shift of the chlorine substituent. The equilibrium isomer mixture is composed of 4% *ortho*, 64% *meta*, and 32% *para*-chlorofluorobenzene. Isomerization of *ortho*-chlorofluorobenzene is much slower than that of the *meta* and *para* isomers (because of the *ortho* deactivating effect of fluorine). Halogen exchange and electrophilic arylation in this case overtake isomerization, so that equilibrium cannot be reached from the *ortho* isomer. Isomerization of dichlorobenzenes also takes place by a predominantly intramolecular 1,2-shift mechanism (disproportionation is generally less than 1%). The equilibrium mixture for dichlorobenzene was found to contain 8% *ortho*, 60% *meta*, and 32% *para* isomer. Difluorobenzenes are unable to undergo Friedel-Crafts isomerization. Halogen exchange and electrophilic arylation are the only reactions taking place. The mechanism of the investigated reactions is discussed based on the obtained experimental data.

The chlorination of benzene and chlorobenzene in the presence of Friedel-Crafts type metal halide catalysts always resulted in the formation of dichlorobenzenes containing besides larger amounts of the *ortho* and *para* isomers also some *meta*-dichlorobenzene. The extent and the cause of the *meta* substitution has not been agreed upon for a long time. Holleman and van der Linden² noticed in 1910 that the proportion of the *meta* isomer increased with increasing reaction time in the aluminum chloride-catalyzed chlorination of chlorobenzene. More recent patent literature contains data on optimum conditions to carry out isomerization of dichlorobenzenes with aluminum chloride and related catalysts.³ The most detailed investigation so far in the literature on the isomerization of dichlorobenzenes is that of Spryskov and Erykalov.⁴ They found that the equilibrium mixture of dichlorobenzenes obtained by heating any of the three isomers with aluminum chloride above 100°, contains about 16% *ortho*, 54% *meta*, and 30% *para* isomer. Analysis of the isomers was carried out by the use of a freezing point method. No data are available to date concerning the Friedel-Crafts isomerization of chlorofluorobenzenes or on the effect of aluminum halides on difluorobenzenes.

In continuation of previous work on the isomerization of halobenzenes¹ it was felt of some interest to reinvestigate the isomerization of dichlorobenzenes and to extend the investigations also to the chlorofluorobenzenes and difluorobenzenes. The availability of gas-liquid chromatographic analysis for the determination of the isomer ratios not only facilitated the investigations, but also allowed to obtain reliable quantitative data, not always obtainable by analytical methods used in previous work.

Results and Discussion

Difluorobenzenes.—The treatment of the isomeric (*ortho*, *meta*, and *para*) difluorobenzenes with water-promoted aluminum chloride under conditions similar to those described previously for the isomerization of halobenzenes,¹ yielded only isomeric chlorofluorobenzenes and dichlorobenzenes besides unidentified tarry materials. Gas-liquid chromatography, which under our experimental conditions had a sensitivity of 1 part per 1000 for isomeric difluorobenzenes, was unable to detect any isomerization of the three difluorobenzenes even after severe treatments (reaction times as long as fourteen days and temperatures up to 240°), converting up to 90% of the starting materials.

The isomeric chlorofluorobenzenes and dichlorobenzenes present in the reaction mixtures were obviously formed by halogen exchange between difluorobenzenes and aluminum chloride (similar to

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