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. × 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 Linden[2] 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 halobenzenes[1] 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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[1] Part I, *J. Org. Chem.*, **27**, 3441 (1962).

[2] A. F. Holleman and T. van der Linden, *Chem. Zentr.*, 1910 II, 640, T. van der Linden, *Rec. trav. chim.*, **30**, 328 (1911).

[3] J. T. Fitzpatrik, U. S. Patent 2,666,085; Brit. Patent 699,153. L. A. Mattano, U. S. Patent 2,727,075. J. W. Angelkorte, U. S. Patent 2,920,109; Can. Patent 541,673; Brit. Patent 723,592.

[4] A. A. Spryskov and Yu. G. Erykalov, *J. Gen. Chem. USSR*, **28**, 1637 (1958); **29**, 2798 (1959).

TABLE I

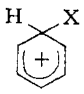
EFFECT OF WATER-PROMOTED ALUMINUM CHLORIDE ON DIFLUOROBENZENES

Temp., °C.	Time, days	Reaction conditions	% Difluorobenzene			% Chlorofluorobenzene			% Dichlorobenzene		
			Ortho	*Meta*	*Para*	*Ortho*	*Meta*	*Para*	*Ortho*	*Meta*	*Para*
93	2	Reflux	100.0	0.0	0.0	5.0	0.1	0.0			
150	14	Sealed tube	100.0	0.0	0.0	5.1	0.8	Trace		Trace	
240	2	Autoclave	100.0	0.0	0.0	8.1	1.5	0.4	0.4	2.3	0.8
83	2	Reflux	0.0	100.0	0.0	0.1	1.7	0.0			
150	14	Sealed tube	0.0	100.0	0.0	Trace	6.4	0.5		Trace	
88	2	Reflux	0.0	0.0	100.0	0.0	0.0	1.1			
150	14	Sealed tube	0.0	0.0	100.0	Trace	0.4	3.3		Trace	

that observed with fluorobenzene[1]) and subsequent isomerization of chlorofluorobenzenes and dichlorobenzenes (as will be discussed later in this paper). Electrophilic arylation yielding substantial amounts of halobiphenyls was also observed in all experiments. Supposedly both halogen exchange and arylation occur according to the previously suggested[1] π-complex mechanism.

The results of experiments on the effect of water-promoted aluminum chloride on difluorobenzenes are summarized in Table I.

Similarly to the previously observed inability of ring-bonded fluorine for intermolecular isomerization (disproportionation),[1] it must be concluded that ring-bonded fluorine is also unable to undergo intramolecular isomerization under Friedel-Crafts conditions. The same observation as with aluminum chloride was also made with a variety of other catalysts, including aluminum bromide, ferric chloride, ferric bromide, gallium chloride, zirconium chloride, etc. The cause of the inability of difluorobenzenes to undergo Friedel-Crafts isomerization must again originate in the fluorine substituent, which not only is unable to form a positive ion but seemingly also a positively polarized entity, generally necessary to achieve intramolecular isomerization by a 1,2-shift mechanism. A further cause may be found in the strong −I effect of the fluorine substituent, which—although it is opposed by the +T conjugative effect—causes a certain electron deficiency. As it is believed that a prerequisite of any isomerization is the protonation of the carbon atom carrying the substituent to be loosened,



this effect in itself should cause a serious difficulty in loosening the C—F bond, which does not seem to be able to lose (even partially) the fluorine as a positively polarized movable entity.

A further, although perhaps less important factor may be the lower basicity of difluorobenzenes, not favoring ring protonation. The question of relative basicity of halobenzenes was treated previously.[5] No data were, however, available on relative basicities of dihalobenzenes.

In order to gain information relating to the relative order of basicity of dihalobenzenes (as compared also with benzene and halobenzenes), similar to previous investigations the shift of the fundamental infrared stretching frequency of hydrogen chloride was measured in different dihalobenzenes. (In order to avoid solvent interferences only liquid dihalobenzenes were investigated.)

A double beam infrared grating spectrophotometer (Perkin-Elmer Model 221-G) employing rocksalt prisms was used. The observed data are shown in Table II.

TABLE II

INFRARED H—Cl STRETCHING FREQUENCY IN DIHALOBENZENES, CM.$^{-1}$

Benzene	2758 ± 2
—benzene, iodo	2761 –
1,2-Iodobromo	2761 –
Bromo	2770 –
Chloro	2775 –
1,2-Dibromo	2779 –
1,2-Iodochloro	2780 –
1,3-Dibromo	2783 –
1,2-Bromochloro	2785 –
1,3-Iodochloro	2790 –
1,3-Bromochloro	2794 –
1,2-Dichloro	2795 –
1,3-Dichloro	2795 –
1,3-Fluoroiodo	2797 –
1,4-Fluoroiodo	2802 –
1,2-Fluorobromo	2808 –
1,3-Fluorobromo	2809 –
1,4-Fluorobromo	2810 –
Fluoro	2810 –
1,2-Fluorochloro	2816 –
1,3-Fluorochloro	2816 –
1,4-Fluorochloro	2818 –
1,3-Difluoro	2828 –
1,4-Difluoro	2829 –
1,2-Difluoro	2830 –
Carbon tetrachloride	2830 –

As expected, in accordance with the −I > + T effect of the halogen substituents, the decreasing order of basicity of dihalobenzenes involved in the present investigation was found based on the decreasing shift of the HCl stretching frequency:

$$C_6H_4Cl_2 > C_6H_4ClF > C_6H_4F_2$$

Thus difluorobenzenes are the least basic dihalo-

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

TABLE III

ISOMERIZATION OF CHLOROFLUOROBENZENES WITH WATER-PROMOTED ALUMINUM CHLORIDE

Starting material	Temp., °C.	Time, days	Reaction condition	% Chlorofluorobenzene			% Dichlorobenzene[a]		
				Ortho	*Meta*	*Para*	*Ortho*	*Meta*	*Para*
o-C_6H_4ClF	134	3	Reflux	89.2	8.1	2.7	Not determined		
	120	14	Sealed tube	42.9	38.5	18.6	1.7	6.0	2.4
	150	7	Sealed tube	37.4	39.4	23.2	2	30	10
	180	10	Sealed tube	50.6	32.9	16.5	5.2	24.9	7.3
m-C_6H_4ClF	128	3	Reflux	0.0	88.9	11.1	0.0	19.0	3.0
	120	14	Sealed tube	1.9	66.4	31.7	0.5	8.5	3.4
	150	7	Sealed tube	3.6	65.0	31.4	2.0	18.3	9.1
p-C_6H_4ClF	131	3	Reflux	0.0	4.7	95.3	0.0	2.1	21.7
	120	14	Sealed tube	3.1	65.6	31.3	Trace	3.0	5.0
	150	7	Sealed tube	2.9	64.6	32.5	1.1	18.8	9.3

[a] The amount of dichlorobenzenes in Tables III and IV is given relative to that of the sum of chlorofluorobenzenes.

benzenes and protonation accordingly should not be favored.

Chlorofluorobenzenes.—Data obtained on the water-promoted aluminum chloride-catalyzed isomerization of the isomeric chlorofluorobenzenes are summarized in Table III.

In all experiments substantial amounts of halobiphenyls and unidentified tarry materials were formed which were not further investigated.

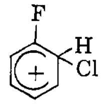
Based on previous observations that ring-bonded fluorine is unable to undergo either intra- or intermolecular migration, the observed data must be interpreted as migration of the chlorine substituent.

From data of Table III, it is quite obvious that the isomerization follows an intramolecular 1,2-shift mechanism. The formation of *p*-chlorofluorobenzene from the *ortho* isomer (and similarly that of the *p*-dichlorobenzene from the *ortho*, as will be discussed in more detail subsequently) takes place only after a substantial amount of the *meta* isomer is first formed. Similarly, the formation of *o*-chlorofluorobenzene from the *para* isomer is substantially delayed with the first formation of a high amount of the *meta* isomer.

Further evidence for the intramolecular nature of the isomerization is the fact that disproportionation to benzene and trihalobenzenes was observed only in trace amounts (less than 1% of the recovered dihalobenzene isomers) even after reaction times as long as several days.

From the data of Table III, it is also to be seen that isomerization of *o*-chlorofluorobenzene is much slower than that of the *meta* or *para* isomers. The equilibrium composition of about 4% *ortho*-, 64% *meta*-, and 32% *para*-chlorofluorobenzene can be reached only from the *meta* and *para* isomers, but not from the *ortho* isomer, even after ten days reaction time at 180°. Halogen exchange and electrophilic arylation reactions (giving rise to halobiphenyls)[6] seem to overtake the velocity of the isomerization reaction. A similar observation in the case of the isomerization of *o*-fluorotoluene will be discussed in a subsequent paper.

The reason for the low reactivity of the *o*-chlorofluorobenzene in the isomerization reaction is in our opinion due to the electronic deactivating effect of the *o*-fluoro substituent on the chlorine undergoing migration. The −I > +T effect of fluorine, as pointed out previously, is the strongest in the neighborhood of the fluorine substituent and is diminishing with the distance, allowing in the farthest *para* position substantial electrophilic reactivity. Since to enable migration of the chlorine substituent an intermediate state corresponding to the benzenonium ion is needed, it is easily understandable



why in positions *ortho* to the fluorine atom, although the steric hindrance is only small, practically no protonation is expected.

The reverse reaction, the formation of the *ortho* isomer, is similarly slow. As shown by the results of all experiments the chlorine atom migrates from the *meta* position faster to the *para* than to the *ortho* position. However, in this case steric considerations must also play a role.

To prove, that the equilibrium mixture obtained of 4% *ortho* , 64% *meta*-, and 32% *para*-chlorofluorobenzene is indeed the correct thermodynamically controlled equilibrium, although obtainable only from the *meta* and *para* isomers for reasons discussed previously, a synthetic mixture of approximate composition was prepared from the pure isomers. Treatment of this synthetic mixture with aluminum chloride at 180° for periods up to fourteen days produced no change in the isomer distribution over the equilibrium values, although halogen exchange and other secondary reactions giving rise to biphenyls and tarous materials obviously were proceeding. Table IV shows the results of the treatment of the synthetic equilibrium mixture of chlorofluorobenzenes with aluminum chloride.

Dichlorobenzenes.—Isomerization of *ortho*-, *meta*-, and *para*-dichlorobenzenes with water-promoted aluminum chloride was carried out at 150° in sealed glass tubes. The obtained results are

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(6) G. A. Olah, 140th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1961, Abstract of Papers, p. 12M.

TABLE IV

TREATMENT OF SYNTHETIC CHLOROFLUOROBENZENE EQUILIBRIUM MIXTURE WITH WATER-PROMOTED ALUMINUM CHLORIDE AT 180°

Time, days	Chlorofluorobenzene *Ortho*	*Meta*	*Para*	Dichlorobenzene *Ortho*	*Meta*	*Para*
0	4.5	61.3	35.2	0	0	0
2	4.4	62.8	32.8	0	Trace	Trace
7	3.9	63.5	32.6	0	6.3	0.9
14	4.2	63.7	32.1	μ	11.4	2.9

shown in Fig. 1–3, as the plots of isomer distributions against reaction times. The composition of the final, equilibrium dichlorobenzene isomer mixture, obtained from all three isomers, was about 8% *ortho*-, 60% *meta*-, and 32% *para*-dichlorobenzene. This composition differs from that reported by Spryskov and Erykalov[4] as the equilibrium dichlorobenzene isomer mixture insofar as the *ortho* isomer is lower and the *meta* isomer higher. Differences observed could be partly due to incomplete isomerization or analytical difficulties in previous work (freezing point method as compared with gas-liquid chromatography used in present investigations).

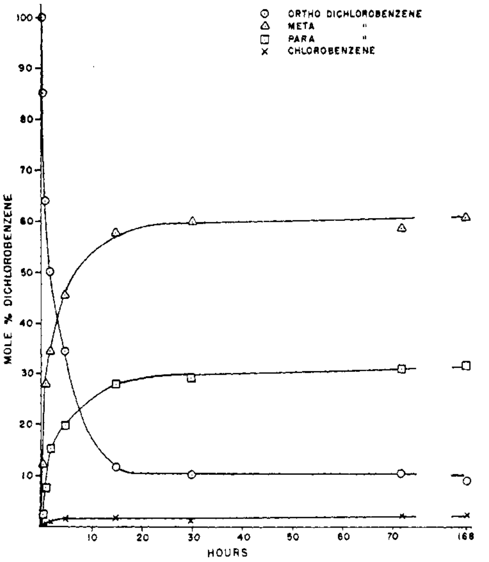


Fig. 1.—Isomerization of *o*-dichlorobenzene with Al_2Cl_6 + H_2O co-catalyst; temp., 150°.

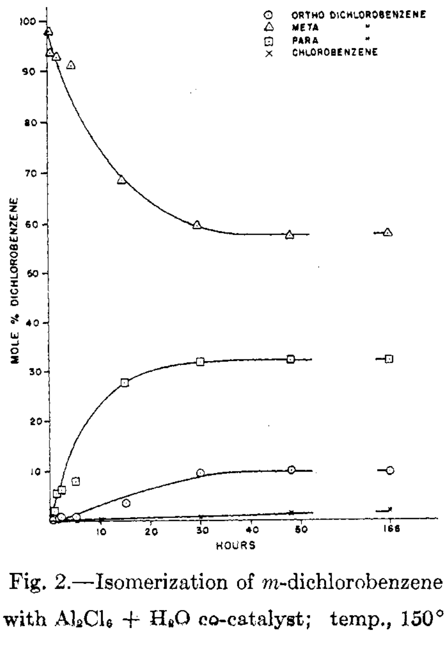


Fig. 2.—Isomerization of *m*-dichlorobenzene with Al_2Cl_6 + H_2O co-catalyst; temp., 150°.

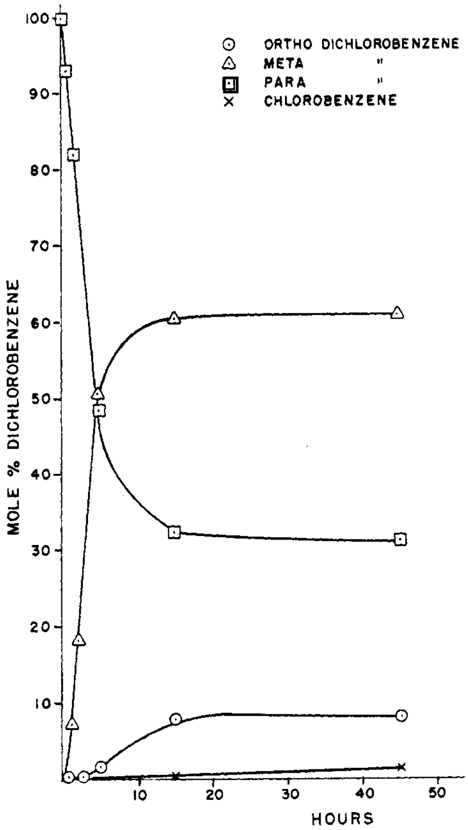


Fig. 3.—Isomerization of *p*-dichlorobenzene with Al_2Cl_6 + H_2O co-catalyst; temp., 150°.

To check that our final isomer distributions (obtained generally after fifteen to twenty hours and not changing thereafter up to reaction times of one hundred and sixty-eight hours) are indeed the thermodynamically controlled equilibrium of the isomeric dichlorobenzenes, again a synthetic mixture of approximate composition was prepared from the pure isomers. This synthetic mixture was then treated with water-promoted aluminum chloride at 200°. As shown in Table V, the composition of the mixture was unchanged even after treatment for fourteen days, thus representing the equilibrium dichlorobenzene composition.

As seen from data of Table V, besides intramolecular migration of the chlorine substituent there is also a certain degree of intermolecular disproportionation. The amount of chlorobenzene obtained after prolonged reaction times is smaller than the amount of trichlorobenzenes formed, probably because of losses leading to higher molecular weight and tarry materials formed more easily from chloro-

TABLE V

TREATMENT OF SYNTHETIC DICHLOROBENZENE EQUILIBRIUM MIXTURE WITH WATER-PROMOTED ALUMINUM CHLORIDE AT 200°

Time, days	Chlorobenzene	Dichlorobenzene			Trichlorobenzene		
		Ortho	*Meta*	*Para*	1,2,3-	1,2,4-	1,3,5-
0	0.4	9.0	56.8	34.2	0	0	0
2	1.6	8.8	58.3	32.9	Trace	1.6	1.0
7	2.0	8.0	59.3	32.7	Trace	8.5	3.7
14	2.6	7.9	59.5	32.6	0.7	11.0	5.3

benzene than from trichlorobenzenes. Disproportionation taking place at 150° during the first twenty-four hours (sufficient to reach isomer equilibrium) is, however, less than 1% and therefore has no particular effect on the investigation of the intramolecular isomerization. In control experiments carried out in the presence of chlorobenzene the disproportionation could be entirely suppressed, but no differences in dichlorobenzene isomerizations were observed.

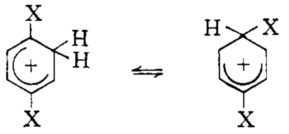
Intramolecular isomerization of dichlorobenzenes as seen from data of Fig. 1–3, proceeded by a 1,2-shift mechanism. This is particularly seen starting from pure *p*-dichlorobenzene (Fig. 3) or pure *o*-dichlorobenzene (Fig. 1). The formation of the *ortho* and *para* isomers, respectively, are considerably delayed until a significant amount of *meta* isomer is formed. This proves that the formation of *ortho* from *para* and *para* from *ortho* isomer is directly dependent on the presence of *meta* isomer and only indirectly on the third isomer. It should be pointed out that although Spryskov and Erykalov[4] have not obtained the real equilibrium composition, they pointed out correctly from their data a similar conclusion concerning the 1,2-shift mechanism of intramolecular dichlorobenzene isomerization.

The trichlorobenzenes formed in present investigations showed an equilibrium composition of about 4% 1,2,3-, 65% 1,2,4-, and 31% 1,3,5-trichlorobenzene. However, no attempt was made to establish whether this is the thermodynamic composition, which in the case of trialkylbenzenes generally shows a higher 1,3,5-isomer distribution. The question of trihalobenzene isomerizations will be discussed in more detail in a forthcoming publication of this series.

The pattern of the 1,2-shift, intramolecular migrating ability of chlorine substituents in Friedel-Crafts isomerizations resembles the similar pattern of methyl group migrations. In contrast the intermolecular migrating pattern of bromine substituents (to be discussed in subsequent papers) is similar to the behavior of the isopropyl and *tert*-butyl groups in Friedel-Crafts isomerizations.

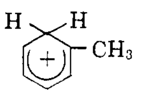
Isomerization of dichlorobenzenes with heavy water–pretreated aluminum chloride catalysts, like previous investigations in the case of the disproportionation of halobenzenes,[1] has shown that ring deuteration always accompanies the isomerizations. Therefore, it must be suggested that present isomerizations also involve a σ-complex type activated intermediate state.

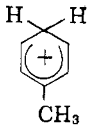
Primary protonation in the σ-complex formations follows electrophilic directing effects in aromatic substitutions (*para-ortho* to the halogen substituent) as shown by n.m.r. investigation of the fluorobenzene–hydrogen fluoride–antimony pentafluoride complex.[7] However, these primary σ-complexes (I) are generally unreactive to isomerization. The activated state in which isomerization takes place is one in which the proton is moved over to a carbon atom carrying the halogen (II).



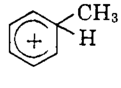
I II

That primary protonation leading to σ-complex formation, with the proton entering the ring according to typical electrophilic substitutions in the *ortho-para* positions, is not itself the "loosening-step" in isomerizations was demonstrated in the case of alkyl- and dialkylbenzenes.[8] A number of alkyl- and dialkylbenzenes (toluene, ethylbenzene, xylenes, mesitylene) formed σ complexes with HF + BF_3 according to a previously described technique.[9] If the σ-complexes were prepared, kept, and decomposed by alcohol or other strong proton acceptors at low temperatures, the starting alkyl(dialkyl)-benzenes could be recovered practically unchanged without any isomerization (with exception of *tert*-butyl and isopropyl groups). Thus it seems that the alkyl substituents (first of all methyl groups) were not sufficiently "loosened" to enable migration. The σ-complexes as shown previously are fairly stable entities themselves, with considerable delocalization (resonance) stabilization. The high stability is mainly due to conjugative stabilization by alkyl groups *ortho* and *para* to the introduced proton in the benzenonium ions. Consequently the





isomerization step must involve an activated state with higher activation energy, which probably is the state where the proton is moved over to a carbon carrying a substituent group.



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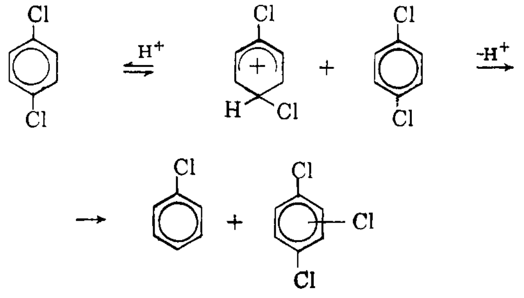
(7) G. A. Olah, E. B. Baker, and W. S. Tolgyesi, unpublished results, G. A. Olah, Abstracts of Papers, 138th ACS Meeting, New York, September, 1960, p. 3P.

(8) G. A. Olah and S. J. Kuhn, unpublished results.

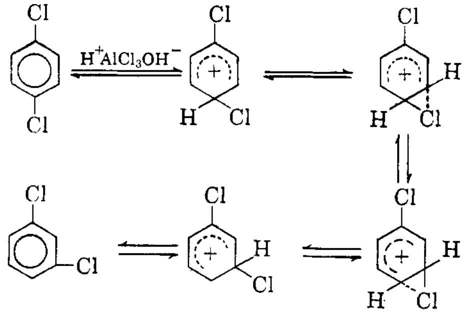
(9) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6535 (1958).

In this transition state the substituent is sufficiently loosened to be able to undergo migration. The more stable the positively charged loosened substituent, the larger is the possibility that it can indeed separate from the original ring as a cationic species, thus effecting disproportionating (intermolecular isomerization). This is the case with isopropyl and *tert*-butyl groups, as well as bromine atoms. Chlorine atoms, like methyl and ethyl groups, however, have little tendency to form a positive, relatively stable species. Therefore, in these cases predominant intramolecular migration takes place with little disproportionation. The disproportions do not, however, really necessitate formation of a free halonium ion, as it is more plausible that displacement of the halogen from the primarily formed σ-complex by nucleophilic attack of a second molecule of halobenzene precedes the complete elimination of a free halonium ion. However, the displaced halogen must be at least partially positively charged.



Concerning the nature of the 1,2-shift mechanism of the intramolecular migration of chlorine atoms in chlorofluorobenzenes and dichlorobenzenes, we suggest a mechanism involving a halogen bridged activated state. A somewhat similar mechanism was suggested for the isomerization of chloronaphthalenes by Vorozhtsov[10] and for chloronaphthalenes by Weingarten,[11] however localizing the positive charge on the bridged halogen, which we do not feel justified in doing, the halogen being part of a conjugated system.

In the above suggested mechanism the halogen never detaches itself from the aromatic ring. At the same time the migrating halogen is acquiring at least a partial positive charge, which could explain why fluorine is unable to take part in similar 1,2-shifts. As the initiation of the migration involves protonation of the carbon atom carrying the halogen to be moved, this explains why the *ortho* and *para* halogens are shifting more easily (conjugative stabilization by halogen substituent facilitates protonation and formation of the intermediate σ-complex) and why the *meta* isomer builds up. The high *meta* isomer content of the equilibrium mixture is, however, a consequence of thermodynamic and not kinetic factors.



Experimental

Materials.—The dihalobenzenes used were commercially available chemicals of highest purity which were further purified by fractional distillation on an Aldershaw column rated for 50 theoretical plates or by preparative scale gas-liquid chromatography. Purity of the purified materials was 99.5% or higher as determined by gas-liquid chromatography.

Aluminum chloride (Fisher, reagent grade) was purified by vacuum sublimation.

Experimental Technique. (a) Experiments Carried Out under Reflux Conditions.—Aluminum chloride (0.05 mole.) and water (1 ml.) were added to 0.5 mole of dihalobenzene. The mixture was refluxed for a period of time given in the tables for each experiment and after cooling was poured on crushed ice. The organic material was extracted with ether, filtered, and freed from acid by washing with small amounts of water three times. After drying over calcium chloride the products were analyzed by gas-liquid chromatography.

(b) **Experiments Carried Out in Closed System.**—The reaction mixtures of the same composition as given above were either sealed in a heavy-wall Pyrex glass tube and heated in an oven or placed in a glass lined thermostatically controlled autoclave. After a certain period of time shown in the tables, the products were cooled and worked up as described above.

Analytical Procedure.—Gas-liquid chromatography was carried out on a Perkin-Elmer Model 154-C Vapor Fractometer using a thermistor detector, equipped with a Perkin-Elmer Model 194 electronic printing integrator. A four

TABLE VI

RETENTION TIMES OF MONO- AND DIHALOBENZENES

Compound	Column temperature, °C.	Retention time, min.
Benzene	70	17
Fluorobenzene	70	20
Chlorobenzene	150	8
o-Difluorobenzene	70	26
m-Difluorobenzene	70	23
p-Difluorobenzene	70	24
o-Chlorofluorobenzene	150	9
m-Chlorofluorobenzene	150	7
p-Chlorofluorobenzene	150	8
o-Dichlorobenzene	150	22
m-Dichlorobenzene	150	17
p-Dichlorobenzene	150	19

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[10] N. N. Vorozhtsov, Jr., and V. A. Koptyug, *J. Gen. Chem. U.S.S.R.*, **28**, 372 (1958).

[11] H. Weingarten, Paper presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, abstr. p. 56-Q.

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.

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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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