Experimental

Photolysis.—In a 1.5-l. quartz reaction vessel, 20-μl. samples of cyclopropylphenylmethane (Aldrich Chemical Co.) were frozen out at Dry Ice temperatures and the system was evacuated. The system was then closed, either by a vacuum stopcock or by sealing off a glass tube, and irradiated for 1 hr. Photolyses were carried out in a Rayonet reactor (Southern New England Ultraviolet Co.) which has previously been described.[8] Radiation wave length was primarily 2537 Å.; reaction temperatures were maintained at 55 and 85°.

The condensable products were frozen out at liquid nitrogen temperature and sealed in tubes, several of which were then opened and combined, using ether as solvent, for analysis. Benzene, toluene, ethylbenzene, and styrene were identified by vapor chromatography retention times (on a 12-ft. di-*n*-decyl phthalate column, 140°), and, except for styrene, also by mass spectral analysis which was completely unambiguous.[9] For gas analysis the reaction vessel was connected to a conventional vacuum system. Condensables were trapped at Dry Ice–acetone temperature; gases were then collected and compressed, by use of a mercury diffusion pump and Toepler pump, into a sample cell connected to a flame ionization gas chromatograph. Gases were identified by comparison of retention times and coinjections with standards on a 3-ft. silica gel column and a 12-ft. β,β'-oxydipropionitrile column, both at room temperature. All C_1–C_3 and several C_4 hydrocarbons were tested and no two of these gases had identical retention times under our conditions.

In some runs 50 mm. of oxygen was bled in prior to irradiation. Identification of gaseous and condensable products was handled the same as in the runs without oxygen except that condensables were analyzed on a tricresyl phosphate column at 50°.

A sample of cyclopropylphenylmethane was degassed and treated identically except that irradiation was omitted. Analysis of any possible gaseous products showed that no reaction ensued under the reaction conditions (85°, 1 hr.).

Pyrolysis.—Samples of cyclopropylphenylmethane were frozen in 5-ml ampoules, evacuated, and sealed off to a fine tip to serve as a break-seal. Samples of 10 μl. were used for quantitative runs and 50 μl. for product analysis. The tubes were heated in a furnace at 400° for 20 hr. The tubes were then placed in a larger vessel which was then evacuated. The vessel was agitated to effect breakage of the ampoule, and attached to the vacuum system for analysis of the gas, such analyses being similar to those described for the photochemical reactions. For quantitative yields all of the gas was compressed into the sample cell and the total gas formed in the reaction determined.

The liquid condensables were analyzed by gas chromatography under the same conditions employed in analysis of corresponding photochemical products. Naphthalene was also analyzed by gas chromatography (6-ft. Ucon polar, 150°). A portion was collected and identified by comparison of its infrared spectrum with an authentic sample, and by its melting point of 80°.

Acknowledgment.—We wish to thank the Petroleum Research Fund of the American Chemical Society and the National Science Foundation for support of this work.

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[8] G. F. Vesley and P. A. Leermakers, *J. Phys. Chem.*, **68**, 2364 (1964).

[9] We are indebted to Dr. G. P. Happ of the Eastman Kodak Co., for mass spectral analyses and interpretations.

Friedel–Crafts Isomerization. XI.[1] Aluminum Chloride Catalyzed Isomerization of the Haloethylbenzenes

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The isomerization of the isomeric *o*-, *m*-, and *p*-fluoroethylbenzenes, -chloroethylbenzenes, and -bromoethylbenzenes has been investigated with water-promoted aluminum chloride. Fluoroethylbenzenes as well as the chloroethylbenzenes isomerize by an intramolecular 1,2-methyl shift mechanism. *m*-Bromoethylbenzene also isomerizes by an apparent 1,2-shift while the isomerization of *o*- and *p*-bromoethylbenzene involves an initial fast intermolecular bromine migration followed by a considerably slower rearrangement to the equilibrium mixture. The equilibrium isomer distributions consist, in the case of fluoroethylbenzenes, of 36% *ortho*, 52% *meta*, and 12% *para* isomer, in the case of chloroethylbenzenes, of 28% *ortho*, 52% *meta*, and 20% *para* isomer, and, in the case of bromoethylbenzenes, of 24% *ortho*, 56% *meta*, and 20% *para* isomer.

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.

Olah and Meyer[2] as well as Crump and Gornowicz[3] and Kooyman and co-workers[4] previously reported on the aluminum halide catalyzed isomerization of halotoluenes. Our investigation was then extended to the isomerization of haloethylbenzenes. The isomerization of fluoroethylbenzenes and chloroethylbenzenes was not studied previously. Kooyman and co-workers[4] reported the equilibrium composition of the bromoethylbenzenes as consisting of 24–25% *ortho*, 53–54% *meta*, and 22% *para* isomer, without, however, providing any further data to the course of the isomerization.

In the present study, fluoroethylbenzenes, chloroethylbenzenes, and bromoethylbenzenes were isomerized with water-promoted aluminum chloride using gas–liquid chromotography 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 mechanism with which the individual isomers are formed.

Results

The isomerization of haloethylbenzenes through the catalytic effect of water-promoted aluminum chloride was investigated. Experimental conditions were similar to those used in the isomerization of halotoluenes.[2] All isomerizations were carried out at 25°. Results are given as normalized percentages of *ortho*, *meta*, and *para* isomer as a function of time.

Fluoroethylbenzenes.—Tables I–III show the data of isomerization of the three isomeric fluoroethylbenzenes. The equilibrium mixture contained 36%

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[1] Part X: *J. Org. Chem.*, **29**, 2687 (1964).

[2] G. A. Olah and M. W. Meyer, *ibid.*, **27**, 3464 (1962).

[3] J. W. Crump and G. A. Gornowicz, *ibid.*, **28**, 949 (1963).

[4] E. C. Kooyman, *Pure Appl. Chem.*, **7**, 193 (1963); G. J. P. Augustijn, E. C. Kooyman, and R. Louw, *Rec. trav. chim.*, **82**, 965 (1963).

ortho, 52% *meta*, and 12% *para* isomer. The rearranged products contain some fluorobenzene and diethylfluorobenzenes, but not ethylbenzene, indicating that the migrating group is the ethyl group and no fluorine migration takes place. Halogen exchange with the catalyst (aluminum chloride) is also observed to some degree, although at the temperature used (~25°) this is of no major importance.

TABLE I

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *o*-FLUOROETHYLBENZENE

	Normalized % of fluoroethylbenzene		
Time, hr.	*ortho*	*meta*	*para*
0	99.9	<0.1	0.1
1	99.8	<0.1	0.1
4	84.2	13.9	1.9
8	43.2	46.7	10.1
24	41.1	44.9	14.0
36	39.1	49.7	11.2
50	35.4	51.4	13.2
72	36.0	50.7	13.3
144	36.1	51.6	12.3
192	35.9	51.4	12.7

TABLE II

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *m*-FLUOROETHYLBENZENE

	Normalized % of fluoroethylbenzene		
Time, hr.	*ortho*	*meta*	*para*
0	0.7	97.6	1.7
1	1.2	96.7	2.1
2	3.1	93.2	3.7
5	7.2	87.7	5.1
8	19.6	70.6	9.8
12	26.2	63.1	10.7
16	33.1	54.2	12.7
24	36.1	50.8	13.1
36	35.3	51.8	12.9
48	35.7	51.5	12.8

TABLE III

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *p*-FLUOROETHYLBENZENE

	Normalized % of fluoroethylbenzene		
Time, hr.	*ortho*	*meta*	*para*
0	1.1	<0.1	98.9
1	1.3	<0.1	98.7
2	7.3	5.6	87.1
4	11.6	9.8	78.6
6	20.6	15.7	63.7
12	27.6	18.3	54.1
22	32.3	26.1	41.6
30	35.2	29.9	34.9
52	36.2	43.4	20.4
72	35.8	44.8	19.4
144	36.1	49.9	14.0
216	35.4	52.1	12.5

Chloroethylbenzenes.—Tables IV–VI show the course of isomerization of *o*-, *m*-, and *o*-chloroethylbenzenes. The data suggest the isomerization to proceed predominantly by 1,2-shifts. Rearranged products contained as much as 20% chlorobenzene formed by disproportionation. No ethylbenzene was detected, however, in any appreciable amounts, which points to the ethyl group as the main migrating entity. The composition of the final equilibrium mixtures was 28% *o*-, 52% *m*-, and 20% *p*-chloroethylbenzene.

TABLE IV

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *o*-CHLOROETHYLBENZENE

	Normalized % of chloroethylbenzene		
Time	*ortho*	*meta*	*para*
0	97.5	0.2	2.3
10 min.	97.6	0.3	2.1
25	97.8	0.3	1.9
40	97.6	0.5	1.9
1 hr.	97.3	0.8	1.9
1.5	96.1	2.1	1.8
2	93.6	4.5	1.9
2.5	87.3	9.9	2.7
3	73.4	21.0	5.6
3.5	69.6	24.6	5.8
4	53.1	37.2	9.7
5	50.4	39.8	9.8
6	46.7	41.8	11.5
7	41.0	45.5	13.5
16	34.1	51.3	14.6
23	29.1	52.7	18.2
26	29.0	52.5	18.5
31	28.8	51.5	19.7
98	28.3	51.7	20.0

TABLE V

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *m*-CHLOROETHYLBENZENE

	Normalized % of chloroethylbenzene		
Time, hr.	*ortho*	*meta*	*para*
0	5.6	83.0	11.4
1	7.4	79.6	13.0
2	10.3	78.6	11.0
5	15.1	69.3	15.6
8	20.1	62.5	17.4
14	24.6	56.5	18.9
24	28.2	51.7	20.1
36	28.6	51.6	19.8
96	27.8	52.1	20.1

TABLE VI

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *p*-CHLOROETHYLBENZENE

	Normalized % of chloroethylbenzene		
Time, hr.	*ortho*	*meta*	*para*
0	4.3	0	95.7
0.5	3.9	0.8	95.3
1	5.2	1.7	93.1
2	12.4	8.7	78.9
3	21.1	19.1	59.8
4	25.6	28.0	46.4
5	27.8	31.7	40.5
6	28.1	36.6	34.3
7	28.6	39.0	32.4
8	28.6	41.1	30.3
11	28.6	44.9	26.5
14	27.7	46.8	25.5
24	28.1	50.7	21.2
36	27.7	51.5	20.8
96	27.8	51.8	20.4

Bromoethylbenzenes.—Bromoethylbenzenes isomerize much faster than either fluoro- or chloroethylbenzenes. At 25° bromoethylbenzenes reached equilibrium in about 1 hr., the mixture of isomers consisting of 24% *ortho*, 56% *meta*, and 20% *para*-bromoethylbenzene.

Tables VII–IX show the course of isomerization of the bromoethylbenzenes at 25°. It is seen that in the isomerization of *o*-bromoethylbenzene (Table VII) the formation of the *para* isomer is faster than that of the *meta*, with the *para* going through a maximum. Similarly, in the isomerization of *p*-bromoethylbenzene (Table IX) the concentration of the *ortho* isomer goes through a maximum. The mechanism of the aluminum halide catalyzed isomerization of the bromoethylbenzenes thus shows close similarity with the previously investigated case of the isomerization of bromotoluenes.[2]

TABLE VII

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *o*-BROMOETHYLBENZENE

Time	Normalized % of bromoethylbenzene *ortho*	*meta*	*para*
0 min.	98.9	1.0	0.1
5	95.5	1.8	2.7
10	91.1	3.3	5.6
20	77.3	8.2	14.5
30	51.3	22.6	26.1
40	44.3	29.9	25.8
50	28.4	45.1	26.5
1 hr.	26.8	52.1	21.1
1.5	25.0	55.0	20.0
2	24.8	55.1	20.1
3	24.1	56.4	19.5
5	23.7	57.1	19.2

TABLE VIII

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *m*-BROMOETHYLBENZENE

Time	Normalized % of bromoethylbenzene *ortho*	*meta*	*para*
1 min.	0.2	98.5	1.3
2	0.4	97.4	2.2
5	0.5	96.2	3.3
7	2.4	92.4	5.2
10	5.1	86.7	8.2
15	10.5	77.1	12.4
25	19.5	63.4	17.1
40	22.5	59.2	18.3
1 hr.	22.6	58.5	18.9
2	23.2	58.3	18.5
3	24.2	57.0	18.8
5	23.9	56.4	19.7

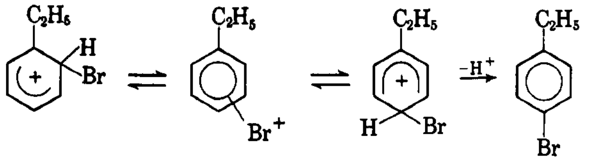
TABLE IX

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *p*-BROMOETHYLBENZENE

Time	Normalized % of bromoethylbenzene *ortho*	*meta*	*para*
0	2.1	2.8	95.1
20 sec.	2.4	5.7	91.9
40	2.6	7.2	90.2
1 min.	3.4	7.5	89.1
2	5.2	9.3	85.5
4	10.3	13.1	76.6
6	16.2	16.7	67.1
10	28.4	21.4	50.2
15	30.0	32.9	37.1
25	27.8	48.2	24.0
40	24.6	54.6	20.8
1 hr.	23.9	55.1	21.0
2	23.8	55.3	20.9
6	24.0	55.4	20.6
30	23.6	55.9	20.5

Isomerization of bromoethylbenzenes under the present conditions is always accompanied by disproportionation. Varying amounts of ethylbenzene and smaller amounts of bromobenzene as well as dibromoethylbenzene and other products of disproportionation were formed in each experiment indicating that the bromo substituent moves preferentially, although ethyl group migration is also a factor. Isomerization of the bromoethylbenzenes in excess benzene led to the formation of appreciable quantities of bromobenzene.

The initial appearance of the *para* isomer in the isomerization of *o*-bromoethylbenzene (and that of *o*-bromoethylbenzene in the isomerization of the *para* isomer) suggests that the bromine atom detaches itself from the protonated bromoethylbenzene, in contrast to the 1,2-shift mechanism, where the migrating group never leaves the aromatic ring. It then rebrominates either excess bromoethylbenzene (resulting in disproportionation) or ethylbenzene formed from the debromination. Bromination of ethylbenzene takes place according to an electrophilic substitution, where it is not necessary to postulate the presence of a free bromonium ion, because the reaction can take place prior to the bromine being entirely detached as a positive entity, ethylbenzene displacing the bromine in the polarized benzenonium ion type activated state. Contribution of a π-complex-like transition state also may have importance. The bromonium species could still remain in a π-complex-type interaction with the ethylbenzene, after severing its σ-bond in the benzenonium ion, and rebrominate intramolecularly according to an electrophilic substitution pattern.



Electrophilic bromination of ethylbenzene gives predominantly *ortho–para* direction, a typical isomer distribution being *ortho* 62.5%, *meta* 1.5%, and *para* 36.2%.[5] Transbromination thus easily can explain the fast initial buildup of the *para* isomer. The formation of *m*-bromoethylbenzene can take place either in a slower 1,2-shift mechanism from both the *ortho* and *para* isomers, or its buildup can result from the fact that the intermolecular bromination–debromination affects preferentially the *ortho* and *para* positions (where it is reversible), but debromination does not effect to any substantial degree the *meta* position (where protonation is not favored). Differentiation between these two possibilities was not attempted in the present work.

A mechanism going through 1,1-di(halophenyl)ethane type intermediates, as suggested in the case of the transalkylation of ethylbenzene by Streitwieser,[6] should also be considered. No observation of 1,1-di(halophenyl)ethane intermediates was made, although they may have been present in the unidentified, high-boiling residues.

In conclusion, the aluminum chloride catalyzed isomerization of the haloethylbenzenes yielded the equilibrium compositions shown in Table X.

When compared with the equilibrium compositions obtained by Olah and Meyer[2] in the Friedel–Crafts isomerization of halotoluenes (Table XI), no specific

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(5) Unpublished results.

(6) A. Streitwieser, Jr., and L. Deif, *J. Am. Chem. Soc.*, **86**, 1988 (1964).

TABLE X

EQUILIBRIUM COMPOSITIONS OF HALOETHYLBENZENES

	% isomeric haloethylbenzene		
	ortho	*meta*	*para*
Fluoroethylbenzenes	36	52	12
Chloroethylbenzenes	28	52	20
Bromoethylbenzenes	24	56	20

TABLE XI

EQUILIBRIUM COMPOSITIONS OF HALOTOLUENES[a]

	% isomeric halotoluenes		
	ortho	*meta*	*para*
Fluorotoluenes	31	56	13
Chlorotoluenes	31	44	25
Bromotoluenes	38	44	18

tendency can be observed. There is evidence of only a slight steric *ortho* effect in the case of the haloethylbenzenes, with the bromoethylbenzenes showing the lowest and the fluoroethylbenzenes the highest amount of *ortho* isomer in equilibrium.

A kinetic evaluation of the isomerization data of the haloethylbenzenes in the present work was not possible, as the reactions are not homogeneous and σ-complex formation may tend to deactivate the catalyst to varying degrees.

Experimental

Materials.—The haloethylbenzenes used, with the exception of the fluoroethylbenzenes, were samples obtained from The Dow Chemical Co., Midland, Mich. Their purity determined by gas chromatography and infrared analysis is shown in the tables. Anhydrous aluminum chloride was reagent grade by Fisher Scientific Co. The fluoroethylbenzenes were prepared by the Schiemann reaction of the corresponding aminoethylbenzenes.

TABLE XII

RETENTION TIMES OF HALOETHYLBENZENES, HALOBENZENES, AND ETHYLBENZENE

Compd.	Column temp., °C.	Retention time, min.	He carrier gas pressure, p.s.i.
Fluorobenzene	40	14	10
o-Fluoroethylbenzene	40	48	10
m-Fluoroethylbenzene	40	53	10
p-Fluoroethylbenzene	40	53.7	10
Chlorobenzene	90	9.8	15
o-Chloroethylbenzene	90	21.8	15
m-Chloroethylbenzene	90	24.2	15
p-Chloroethylbenzene	90	25.0	15
Ethylbenzene	100	6	20
Bromobenzene	100	9	20
o-Bromoethylbenzene	100	21	20
m-Bromoethylbenzene	100	23	20
p-Bromoethylbenzene	100	25	20

General Process of Isomerization.—Reactions were carried out in stoppered flasks with magnetic stirring at ~25°. Two-tenths mole of aluminum chloride/mole of haloethylbenzene was used and 1 ml. of water was added as a promoter. Samples were drawn periodically, the reaction was stopped with water, and the organic material was extracted with ether. The dried ether extracts were analyzed by gas–liquid chromatography.

Results given in tables are normalized % of *ortho*, *meta*, and *para* isomer.

Gas–Liquid Chromatographic Analysis.—Gas–liquid chromatographic analyses were carried out on a Perkin-Elmer Model 226 vapor fractometer equipped with a 150-ft. polypropyleneglycol-coated capillary column and hydrogen flame ionization detector. Column conditions are given together with characteristic retention times in Table XII. Peak areas were directly determined by the use of a high speed electronic Infotronics Model CRS-1 integrator.

The Radiation-Induced Addition Reaction of Ethers to 1,2-Dichlorotetrafluorocyclobutene and 1,2-Dichlorohexafluorocyclopentene

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The addition reactions of tetrahydrofuran, dioxane, and diethyl ether to 1,2-dichlorotetrafluorocyclobutene and 1,2-dichlorohexafluorocyclopentene were carried out under γ-ray irradiation. Though the addition of tetrahydrofuran to 1,2-dichlorotetrafluorocyclobutene gave only the 1:1 adduct in a excellent yield, the addition of dioxane yielded mainly the dehydrochlorinated 1:1 adduct, 2-(2-chlorotetrafluoro-1-cyclobutenyl)-dioxane, along with the 1:1 adduct. In the case of diethyl ether, both the dehydrochlorinated 1:1 and 1:2 adducts, α-(2-chlorotetrafluoro-1-cyclobutenyl)diethyl ether and α-(1,2-dichlorotetrafluorocyclobutyl)-α'-(2-chlorotetrafluoro-1-cyclobutenyl)diethyl ether, were formed along with the 1:1 and 1:2 adducts. In the addition of the ethers to 1,2-dichlorohexafluorocyclobutene, only the corresponding dehydrochlorinated 1:1 adducts were obtained.

The nucleophilic additions of alcohols to fluorine-containing cyclobutene[1] and cyclopentene[2] in the presence of base to give ethers with polyfluorocycloalkyl groups have been investigated by several workers. So far as we know, no report on the synthesis of ethers containing polyfluorocycloalkyl groups by free-radical reaction has appeared in the literature.

This paper presents the addition reaction of ethers, such as tetrahydrofuran, dioxane, and diethyl ether, to 1,2-dichlorotetrafluorocyclobutene and 1,2-dichlorohexafluorocyclopentene under γ-ray irradiation. A mixture of the halocyclobutene or halocyclopentene and the ether in a molar ratio of 1:3 was irradiated in a glass tube at a rate of 0.59×10^5 r./hr. for a period of 4 weeks at room temperature (total dosage $4.2–4.3 \times 10^7$ r.).

A previous paper[3] on the γ-ray induced addition of ethers to chlorofluoroethylene reported that only the

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(2) R. A. Shepard, H. Lessoff, J. D. Domijan, D. B. Hilton, and T. F. Finnegan, *J. Org. Chem.*, **23**, 2011 (1958).

(3) H. Muramatsu, K. Inukai, and T. Ueda, *ibid.*, **29**, 2220 (1964).