Ether (20 ml.) and 1.0 ml. of water were added, and the mixture was allowed to stand overnight, during which time the ammonia evaporated. The ether solution was decanted from the solids in the flask, the solids were washed with 20 ml. of ether, and the ether solutions were combined and dried over sodium hydroxide. Most of the ether was removed by distillation through a short, packed column, and the residue was distilled through a semimicro Vigreux column to yield 1.4 g. (65% based on sodium amide) of N-*n*-butylpropargylamine, b.p. 68–70° (102 mm.), n^{28}D 1.4382.

Anal. Calcd. for $C_7H_{13}N$: C, 75.62; H, 11.78; N, 12.60. Found: C, 75.61; H, 11.72; N, 12.50.

Using essentially the same procedure, 40 g. (0.21 mole) of I (72% *cis* and 28% *trans*) and 9.0 g. (0.23 mole) of sodium amide in 400 ml. of liquid ammonia yielded 9.3 g. (73% based on sodium amide, 39% based on I) of N-*n*-butylpropargylamine, b.p. 66–68° (100 mm.), n^{28}D 1.4384. The residue was not examined.

Using essentially the same procedure, but with a larger sodium amide/I mole ratio, 30 g. (0.16 mole) of I (72% *cis*-I) and 13.3 g. (0.34 mole) of sodium amide gave 13.5 g. (76%) of N-*n*-butylpropargylamine, b.p. 66–68° (100 mm.), n^{28}D 1.4384.

The products from the three reactions had identical infrared spectra and identical retention times (344 sec.) on a 1.0 × 200 cm. column packed with nonyl phthalate on firebrick with a flow rate of 110 cc./min. of helium at 120°. GLPC analysis of the concentrated ether solutions from the reactions failed to show the presence of *n*-butylamine (III) or to indicate the presence of IV.

Dehydrobromination of N-(3-Bromoallyl)-*n*-butylamines with Sodium Hydroxide in Aqueous Dioxane.—The reactions of I (*cis* and *trans*) with sodium hydroxide in 50% aqueous dioxane were followed by measuring the bromide ion produced as a function of time. The bromide ion concentration in each aliquot was determined by adding excess standard silver nitrate solution to the cooled acidified aliquot, and titrating the excess silver nitrate with standard potassium thiocyanate solution.[12] Prior to carrying out kinetic runs, samples of *cis*-enriched I (0.0251 *M*) and sodium hydroxide (0.06 *M*) were heated at 77.2° for up to 96 hr. The concentration of bromide ion produced was found to remain constant at 0.0070 *M* after 48 hr. Similar treatment of *trans*-I yielded <3% of the theoretical amount of bromide ion in 48 hr. From this, the initial concentration of *cis*-I in *cis*-enriched I was estimated as 72% of the initial concentration of I. Treatment of a 0.0249 *M* solution of I (72% *cis*-I) containing no sodium hydroxide at 77.2° for 48 hr. failed to produce any bromide ion.

Setting the concentration of hydroxide ion, $(\mathrm{OH^-})_t$, at any time, *t*, equal to the initial hydroxide ion concentration less the bromide ion concentration at *t*, and setting the *cis*-I concentration, $(cis\text{-I})_t$, at *t* equal to the initial *cis*-I concentration less the concentration of bromide ion, good straight line plots were obtained when $\ln [(\mathrm{OH^-})_t/(cis\text{-I})_t]$ was plotted against *t*. Typical plots are shown in Fig. 1. The second-order rate constant, k_2, was calculated for each experimental point using the integrated rate expression for a second order reaction

$$k_2 = \frac{1}{[(\mathrm{OH^-})_0 - (cis\text{-I})_0]} \ln \frac{(cis\text{-I})_0 (\mathrm{OH^-})_t}{(\mathrm{OH^-})_0 (cis\text{-I})_t}$$

The average values for k_2 at 61.4 and 77.2°, together with the calculated Arrhenius energy of activation and the entropy of activation at 61.4° are given in Table I.

Treatment of a 50% aqueous dioxane solution 0.0115 *M* in *trans*-I and 0.065 *M* in sodium hydroxide at 100° for 48 hr. produced 8% of the theoretical amount of bromide ion.

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Isomerization of Bromochlorobenzene Using Aluminum Chloride Catalyst

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Leroy[1] (1887) and Copisarow[2] (1921) reported the isomerization and disproportionation of dibromobenzene. Fairbrother and Scott[3] reported the equilibrium constant for disproportionation in the system bromobenzene, benzene, dibromobenzene to be 0.040 at 25° using aluminum bromide as the catalyst.

The equilibrium mixture for the aluminum halide catalyzed isomerization of dichlorobenzene was reported by Angelkort[4] to be 10–15% *o*-, 55–60% *m*-, and 25–30% *p*-. A small amount of disproportionation was also reported. Spryskov and Erykalov[5] found the equilibrium to be 12% *o*-, 55% *m*-, and 33% *p*-.

It is the purpose of this paper to present data to establish the thermodynamic equilibrium for the bromochlorobenzene system catalyzed by aluminum chloride, and to delineate side reactions. Studies of the kinetics of this and related systems are being published currently by Crump and Gornowicz[6] and by Olah, *et al.*[7–9]

Experimental

All boiling points and melting points are uncorrected.

Materials.—The three bromochlorobenzene isomers were prepared and purified for use as infrared standards and to determine the physical properties. *o*-Bromochlorobenzene was synthesized from *o*-bromoaniline [Distillation Products Industries, white label] using the hot procedure Sandmeyer reaction described by Fry and Grote,[10] modified by the substitution of 10 *N* hydrochloric acid for acetic acid. Phenolic impurities were removed by washing the crude product with 2 *N* sodium hydroxide, after which the product was purified by fractional distillation. The product was distilled at 88°/20 mm. to give a yield of 31% based on bromoaniline, and was found to melt at −12.2° (reported freezing point −12.6° −12.1°).[11]

m-Bromochlorobenzene was synthesized from *m*-bromoaniline [Distillation Products Industries, white label] by the procedure described above. The product was distilled at 83°/20 mm. to give a yield of 27.8% based on *m*-bromo-

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TABLE I

PHYSICAL CONSTANTS OF BROMOCHLOROBENZENE ISOMERS

	Bromochlorobenzene		
M.p.	*o*-, −12.2	*m*-, −21.9	*p*-, 67–68
B.p. at 10.00 mm.	75.5	69.0	73.5
30.0 mm.	98.5	95.5	96.0
100 mm.	131.0	126.0	127.0
750 mm.	198.0	196.0	197.0

aniline, and was found to melt at −21.9° (reported freezing point −21.2°).[11]

p-Bromochlorobenzene used was the commercial product of The Dow Chemical Co. Sublimation of a sample of material did not change its melting point (67–68°).

Aluminum chloride used was Baker Adamson, reagent grade, anhydrous sublimed. Aluminum chloride hexahydrated used was Mallinckrodt A.R. grade.

The principal catalyst used consisted of water promoted aluminum chloride in a H_2O/Al_2Cl_6 mole ratio of 1.2. Anhydrous aluminum chloride and aluminum chloride hexahydrate in the correct mole proportion to give this ratio were ballmilled to produce a uniform mixture. During isomerization it was found that hydrogen chloride, equivalent to all of the hydrogen in the water, was evolved. No measurable evolution of hydrogen chloride was obtained using anhydrous aluminum chloride.

TABLE II

ISOMERIZATION OF BROMOCHLOROBENZENE

Conditions: Time, 2.5 hr.; temp., 105–120°; catalyst, 10 mole % ($AlCl_3$ + 0.6 H_2O)

	Mole % charge				Mole % products recovered			Bromochlorobenzene fraction, Wt. of composition			Equiv. inorganic	
	Bromochlorobenzene			Chloro-	Bromo-	Chloro-	Dibromo-				Br^-	Cl^-
Run	*o*-	*m*-	*p*-	benzene	chlorobenzene	benzene	chlorobenzene	*o*-	*m*-	*p*-	Formed	Charged
1			100		65.9	17.6	17.6	4.6	58.5	36.9	0.008	0.132
2			37	63	37.0	63.0	0	0	62.0	38.0	0.006	.132
3			70	30	58.0	35.8	6.2	1.5	66.7	31.8	0.009	.132
4[a]			100		66.1	17.1	16.8	3.0	63.6	33.4	0	.132
5			54	46	52.5	43.1	4.4	0	66.0	34.0		
6	100				70.0	15.3	14.7	2.9	64.2	32.9	0	.132
7	37			63	37.0	63.0	0	6.0	62.0	32.0	0	.132
8		100			68.4	15.4	16.2	4.4	63.3	32.3	0	.132
9		37		63	37.0	63.0	0	5.6	64.2	30.2	0	.132
					average runs 1–9			3.1	63.4	33.5		
10[b]	7.5	0	67.5	25	63.6	31.4	3.2	3.7	63.4	32.9		
11[a,c]	10.5	3.7	57.0	28.7	62.9	31.0	3.3	4.1	63.3	32.6		

[a] Aluminum chloride anhydrous. [b] Conditions, 3 hr., 157°. *Ortho* isomer concentrated by fractional distillation, then analyzed. [c] Sampled during run for reaction rate determination.

Procedure.—Vapor pressure data (not found in the literature) were determined using a semimicro method described in Kamm's "Qualitative Organic Analysis," 2nd ed., p. 128. The vapor pressure data were plotted on a Cox chart. Any value deviating from a straight line on this chart was redetermined. The data obtained and shown in Table I indicate that isomer separation by distillation is favored by low pressure.

Isomerizations were made in a 500-ml. three-necked flask fitted with a stirrer, thermometer, and reflux condenser vented to a scrubber containing standard alkali. The charge, consisting of 0.440 mole of bromochlorobenzene, and if desired, chlorobenzene of known weight, and 0.044 mole of aluminum chloride catalyst, was heated to 105–120° for 2 hr. Any hydrogen halide evolved was determined by analysis of the scrubber liquor for bromide and chloride. The product was steam distilled to a decanter where it was collected, and the water phase was returned to the flask. The product was removed, weighed, and analyzed. The water solution remaining in the flask was measured and analyzed for inorganic bromide and chloride. The isomerization data so obtained (Runs 1–9 and 11) have been summarized in Table II.

The products of isomerization were quantitatively assayed by infrared analysis using a Perkin-Elmer Model 137 Infracord equipped with a Reeder thermocouple. The infrared absorption bands used for analysis of the compounds involved are listed in Table III. Measurements were made in carbon disulfide solution using 0.1-mm. cell.

Accurate analysis of *o*-bromochlorobenzene is difficult when its concentration is less than 5% in the presence of large amounts of chlorobenzene and *m*-bromochlorobenzene because of the difficulty in accurately locating the base line. Interference by the 13.38 μ band of 1,3-dibromo-5-chlorobenzene also occurs. Consqeuently the presence of *ortho* in the combined product from Runs 1–9 was confirmed by fractional distillation, and Run 10 was made to determine the composition more accurately.

Run 10 was made on a 13-mole scale at 157° for 3 hr. to provide material, having equilibrium composition, for the concentration of the *o*-bromochlorobenzene isomer by fractional distillation. This separation was made in a silvered vacuum jacketed column having a 1-inch i.d. by 6-foot section packed with $^1/_8$-inch × 0.015 gage Fenske stainless steel helices. Chlorobenzene (20.9% of charge) was removed using a reflux ratio of 10 (b.p. 56–58°/57 mm.). The bromochlorobenzenes were then separated into two fractions at 10 mm. using a reflux ratio of 100. The fraction which boiled at 71°/10 mm. (60.0% of charge) contained 67.3% *m*- and 32.7% *p*-bromochlorobenzene. The last fraction which boiled at 71–75°/10 mm. (11.6% of charge) contained 43.2% *m*-, 34.0% *p*-, and 22.8% *o*-bromochlorobenzene. Distillation was terminated when the temperature in the still head started to drop due to the lack of vapors, at a pot temperature of 150° leaving 5.7% of the charge as a residue containing less than 1% bromochlorobenzenes. The three fractions and residue account for 98.2% of the charge. The balance was column hold-up and loss.

TABLE III

INFRARED BANDS USED FOR ANALYSIS

	μ	
Chlorobenzene	13.45	14.18
o-Bromochlorobenzene	13.33	
m-Bromochlorobenzene	12.92	13.17
p-Bromochlorobenzene	12.33	
1,2-Dibromo-4-chlorobenzene	12.36	12.81
1,3-Dibromo-4-chlorobenzene	12.36	13.02
1,4-Dibromo-2-chlorobenzene	12.40	12.82
1,3-Dibromo-5-chlorobenzene	12.73	13.38

Discussion

The first isomerization experiment on *p*-bromochlorobenzene showed that there was halide exchange with the catalyst, disproportionation, and isomerization. The nature of disproportionation products depended on the reaction temperature. At reflux (*ca.* 175°) polybromochlorobenzene tars were formed in contrast to relatively pure dibromochlorobenzene formed at temperatures below 155°. Experimental conditions were selected to give a rapid rate of isomerization without tar formation. Equilibrium was approached by isomerizing each pure isomer to ensure accurate values. Any experiment having less than 95 mole % product accounting was repeated to minimize experimental error. The equilibrium mixture so obtained had an average composition of 3.1% *o*-, 63.4% *m*-, and 33.5% *p*-bromochlorobenzene. The equilibrium composition calculated from Run 10 data was 3.7% *o*-, 63.4% *m*-, and 32.9% *p*-bromochlorobenzene, and is in good agreement with the average.

The last experiment in Table II was sampled periodically during isomerization. The composition of each sample was determined and these data are shown in Table IV. The isomer distribution obtained in this experiment was 4.1% *o*-, 63.3% *m*-, and 32.6% *p*-bromochlorobenzene.

TABLE IV

ISOMERIZATION RATE DATA OF BROMOCHLOROBENZENE

Catalyst, Al_2Cl_6: temp. 110°

	Wt. % composition			
		Bromochlorobenzene		
	Chlorobenzene	*o*-	*m*-	*p*-
Charge start heating	19.1	12.1	4.0	64.8
0 min. at temp.	21.5	7.4	27.8	43.3
15	21.8	4.5	43.6	30.1
30	21.6	3.7	46.5	27.2
60	20.8	3.4	48.7	27.1
120	21.4	3.5	49.4	25.7
240	21.2	3.5	49.3	26.0
Cool to 25° during 18 hr.	20.3	3.3	50.4	26.0

The disproportionation products obtained as a residue by distillation of the combined product from the first 9 runs partly crystallized at room temperature. The solid was separated and purified by crystallization from methanol. It was characterized as 1,3-dibromo-5-chlorobenzene by infrared. Its melting point was 95.0–96.0 (reported m.p. 96°; 99.5°)[12] and its identity was further confirmed by elemental analysis. The liquid fraction was determined by infrared spectrum to be a mixture of the three dibromochlorobenzenes having 1,2,4-substitution. The 1,3,5-isomer accounted for 76.7% of the dibromochlorobenzene disproportionation product. No bromochlorobenzenes were detected.

Disproportionation was reduced in an amount predicted by the law of mass action, by the use of chlorobenzene as solvent in replicate isomerizations. Fairbrother and Scott[3] reported 17% disproportionation at the equilibrium. In this work we obtained 15–18% indicating probable approach to equilibrium ($K_{eq} = 0.09$).

Bromine-chlorine exchange occurred during the isomerization of *p*-bromochlorobenzene with water promoted aluminum chloride catalyst, to the extent of 2 mole % on the organic or 20 mole % on the catalyst. No exchange was observed during the isomerization of *o*- or *m*-bromochlorobenzene under identical conditions. Anhydrous aluminum chloride gave no halogen exchange even with the *para* isomer.

It is of interest to compare this isomerization with that of dichlorobenzene. Bromochlorobenzene can be isomerized, without special purification, to equilibrium composition using aluminum chloride with or without water promotion at temperatures as low as 100°. Dichlorobenzene does not isomerize to any extent using anhydrous aluminum chloride at 175°. However, at a temperature of 250° isomerization to equilibrium is obtained, even when technical grade dichlorobenzene is used. When water promoted aluminum chloride catalyst is used, equilibrium isomerization is obtained at 175° provided the dichlorobenzene is pure. The degree of isomerization of dichlorobenzene is very closely related to the trace amount impurities in the dichlorobenzene.

Reaction of Isobutyraldehyde and 2-Ethylhexaldehyde with Ammonium Sulfide. Reductive Thiolation

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The recent report of Harris and Sheppard[2] concerning the reductive thiolation of fluorocarbon carbonyl compounds prompts us to report our results regarding a similar reaction of isobutyraldehyde and 2-ethylhexaldehyde with ammonium sulfide.

The catalytic reductive thiolation of aldehydes and ketones has been investigated[3] and is reported to be effected only in the presence of sulfactive catalysts.[2] Under Willgerodt conditions,[4,5] cyclohexanone is transformed into cyclohexanethiol and

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