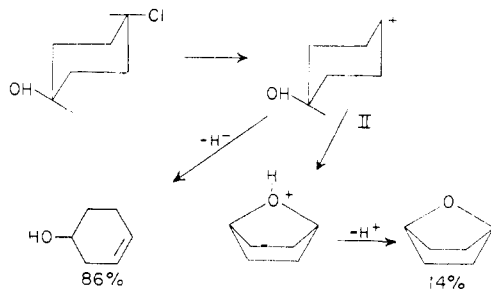


cyclohexanol to the carbonium ion intermediate (II) which subsequently undergoes either ring closure by attack of the hydroxyl group or elimination by expulsion of a proton, *i.e.*



In considering these alternative interpretations, it was of interest to observe in this Laboratory that a 0.003 *M* solution of cyclohexyl chloride at 80° hydrolyzed as rapidly as the *trans*-4-chlorocyclohexanol. It is also to be noted that the acetolysis of cyclohexyl *p*-toluenesulfonate¹⁴ proceeds at a comparable rate to the *trans*-4-methoxycyclohexyl tosylate,¹ *viz.*, 4.27×10^{-5} sec.⁻¹ at 74.9° and 3.20×10^{-5} sec.⁻¹ at 75.09°, respectively.

Acknowledgments.—The author wishes to acknowledge the helpful assistance of Gordon F. MacKenzie and Howard Crawford.

(14) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *THIS JOURNAL*, **70**, 816 (1948).

LEWISBURG, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Addition of Hydrogen Bromide to 1-Halocyclohexene and the Rearrangement of Dihalocyclohexanes in the Presence of Ferric Chloride^{1,2}

BY HARLAN L. GOERING AND LESLIE L. SIMS

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The ionic addition of hydrogen bromide to 1-chlorocyclohexene and 1-bromocyclohexene in excess liquid hydrogen bromide in the presence of a small amount of ferric chloride gives 1-bromo-1-chlorocyclohexane and 1,1-dibromocyclohexane, respectively. In the presence of larger amounts of ferric chloride the initially formed *gem*-dihalide undergoes halogen exchange and rearrangement. Thus both 1-chlorocyclohexene and 1-bromocyclohexene can be converted to *trans*-1,4-dibromocyclohexane in good yields. Examination of products from a series of experiments in which the amount of ferric chloride was varied indicates the following sequence for the conversion of 1-chlorocyclohexene to *trans*-1,4-dibromocyclohexane: 1-chlorocyclohexene → 1-bromo-1-chlorocyclohexane → 1,1-dibromocyclohexane → *cis*-1,2-dibromocyclohexane → 1,3-dibromocyclohexane → *trans*-1,4-dibromocyclohexane. Apparently, *trans*-1,2-dibromocyclohexane is not involved as an intermediate in this process. Under appropriate conditions 1-chlorocyclohexene can be converted to 1-bromo-1-chlorocyclohexane, 1,1-dibromocyclohexane or *trans*-1,4-dibromocyclohexane in good yields.

Introduction

The ionic addition of hydrogen bromide to 1-halocyclohexene in the presence of small amounts of anhydrous FeCl₃ in excess liquid hydrogen bromide proceeds rapidly at low temperature and gives the normal addition product. Thus 1-chlorocyclohexene (I) and 1-bromocyclohexene are converted to 1-bromo-1-chlorocyclohexane (II) and 1,1-dibromocyclohexane (III), respectively, in good yields.³ However, in the presence of larger amounts of FeCl₃ the initially formed *gem*-dihalide undergoes halogen exchange and rearrangement. Indeed, our first attempts to prepare 1-bromo-1-chlorocyclohexane from I by the addition of hydrogen bromide in the presence of FeCl₃ resulted instead in the formation of *trans*-1,4-dibromocyclohexane (VI), isolated in pure form in yields of about 80%. Similarly, 1-bromocyclohexene was converted to VI. This paper describes an investigation of the halogen exchange and rearrangement involved in the conversion of I and 1-bromocyclohexene to VI.

(1) This work was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF18(600)-1037 and in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(2) Abstracted from the doctoral dissertation of Leslie L. Sims, University of Wisconsin, 1955.

(3) H. L. Goering and L. L. Sims, *THIS JOURNAL*, **77**, 3465 (1955).

Results

To obtain information concerning intermediates involved in the conversion of 1-chlorocyclohexene (I) to *trans*-1,4-dibromocyclohexane (VI), a number of experiments was carried out in which the amount of FeCl₃ was varied. The results of these experiments are summarized in Table I. In these

TABLE I
REACTION OF 1-CHLOROCYCLOHEXENE WITH HYDROGEN BROMIDE IN THE PRESENCE OF FeCl₃^a

Expt.	FeCl ₃ , g.	Product				
		Weight, g.	B.p., °C.	Mm.	<i>n</i> _D ²⁰	Composition
1	0.1	15.3	86-89	26	1.5109	II
2	.4	11.7	60-65	7	1.5082	II
3	.6	15.6	66-74	6	1.5276	II and III
4	.75	16.2	73-78	7	1.5391	III
5	1.0	16.2	91-98	8	1.5499	III, IV, V and VI
6	2.0	17.0				VI
7	2.5 ^b	15.5	60-67	7	1.5100	II and III

^a Ten grams of I and 50 g. of hydrogen bromide were used in all of these experiments; reaction time, 24 hr. ^b Reaction time, 1.5 hr.

experiments 50 g. of solid hydrogen bromide, 10 g. of I and a weighed amount of FeCl₃ were collected in a Pyrex reaction vessel cooled in liquid air. The frozen anhydrous reaction mixture was placed in a bomb and allowed to stand at room temperature for 24 hr. Presumably under these conditions the

reactions occur in the excess liquid hydrogen bromide. The products were identified by comparison of their infrared spectra with those of authentic samples.

Under the conditions described above, with 0.4 g. or less of FeCl_3 (expt. 1 and 2), the normal ionic addition product 1-bromo-1-chlorocyclohexane (II) was isolated in good yield. With larger amounts of FeCl_3 the initially formed normal addition product II undergoes halogen exchange and rearrangement. That exchange precedes rearrangement is shown by experiments 3 and 4. In the latter experiment halogen exchange evidently reached equilibrium—about 85% of the total halogen in the system was bromine and 1,1-dibromocyclohexane (III) was isolated in yields of about 80%—without appreciable rearrangement. Under equilibrium conditions for halogen exchange, *e.g.*, expt. 4, 5 and 6, a small amount of bromochlorocyclohexane must be present. This material evidently was separated from the dibromide fraction by distillation or recrystallization in the isolation procedure.

Experiment 5 is especially informative as far as the mechanism of the rearrangement is concerned. The mixture of dibromocyclohexanes was carefully examined and found to contain 1,1-dibromocyclohexane (III), *cis*-1,2-dibromocyclohexane (IV), 1,3-dibromocyclohexane (V) and *trans*-1,4-dibromocyclohexane (VI). Careful fractionation of a large amount of material obtained from several duplicate experiments gave fractions of nearly pure III and IV. Pure crystalline VI also was isolated. Examination of the infrared spectra of all of these fractions indicated that *trans*-1,2-dibromocyclohexane was not present. The latter dibromide has two characteristic absorption bands which enables detection of about 3% of this compound in the presence of the other dihalides. The configuration of the 1,3-dibromocyclohexane used for comparison and thus that of the material involved in the rearrangement was not established.

In the presence of 2.0 g. (or more) of FeCl_3 (expt. 6) apparently rearrangement as well as halogen exchange reaches equilibrium and the most stable dibromide, *trans*-1,4-dibromocyclohexane (VI), predominates and can be isolated in about 80% yield. Isolation of VI in pure form is facilitated by the fact that it is a crystalline solid, whereas the other dihalides are liquids. Under the conditions of experiment 6 the dihalides formed in the preceding experiments as well as other dihalocyclohexanes are converted to VI as illustrated by the experiments given in Table II. With 2.5 g. of FeCl_3 and a reaction time of 1.5 hr. (expt. 7) the product was found to be a mixture of 1-bromo-1-chlorocyclohexane (II) and 1,1-dibromocyclohexane (III). The experiments included in Table I were found to be qualitatively reproducible and those from which pure products can be isolated readily, *i.e.*, expt. 2, 4 and 6, were repeated several times.

It should be pointed out that the yields reported in Table II are single observations. For this reason, together with the fact that reaction conditions cannot be duplicated exactly by the method used, the relative yields are not considered to be quantitatively significant. The low yield of VI isolated

TABLE II
CONVERSION OF DIHALOCYCLOHEXANES AND 1-BROMOCYCLOHEXENE TO *trans*-1,4-DIBROMOCYCLOHEXANE^a

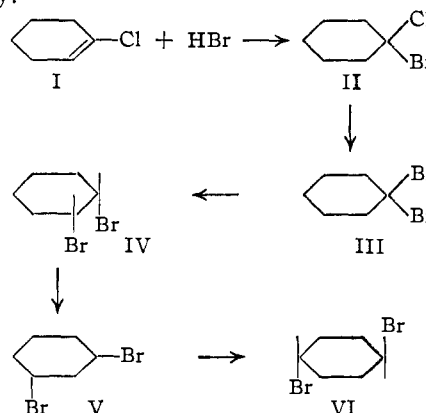
Expt.	Reactant (g.)	Yield of VI g. ^b
8	1-Bromocyclohexene (13.7)	2.2 ^c
9	1,1-Dichlorocyclohexane (13.0)	15.3
10	II (15.8)	17.6
11	III (19.8)	16.3
12	<i>trans</i> -1,2-Dichlorocyclohexane (13.4)	19.4
13	<i>trans</i> -1,2-Dibromocyclohexane (20.6)	18.5
14	V (21.0)	5.6 ^d

^a About 50 g. of HBr and 2 g. of FeCl_3 were used in each experiment; reaction time, 24 hr. ^b Pure VI melts at 112–114°. These yields are for material melting >110°. ^c Fourteen grams of liquid consisting of IV, V and VI were isolated in this experiment. ^d Twelve grams of unreacted V recovered in this experiment.

in experiments 8 and 14 probably is not due to a relatively low reactivity of 1-bromocyclohexene and V but is more likely due to some other variable such as the activity of the catalyst, *e.g.*, moisture in the system would decrease the activity of the catalyst.

Discussion

The data presented in the preceding section suggest that the conversion of 1-chlorocyclohexene (I) to *trans*-1,4-dibromocyclohexane (VI) involves the intermediates shown below. Some of these reactions are presumably reversible under the present conditions; however, the process proceeds in the indicated direction to the extent that when equilibrium obtains, VI can be isolated in about 80% yield. Two of the intermediates, 1-bromo-1-chlorocyclohexane (II) and 1,1-dibromocyclohexane (III), are sufficiently stable so that compound I can be selectively converted to either of them in good yield. The smooth conversion of I to III followed by debromination of the latter provides a preparation for 1-bromocyclohexene (55% yield from I) which is superior to that used previously.^{3,4}



The first step in this process is the ionic addition of hydrogen bromide which is catalyzed by FeCl_3 .⁵ In view of the rapid exchange of halogen between hydrogen chloride and SnCl_4 ⁶ and AlCl_3 ⁷ at low tem-

(4) N. Zelinsky and A. Gorsky, *Ber.*, **44**, 2312 (1911).

(5) F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

(6) R. A. Howald and J. E. Willard, *This Journal*, **77**, 2046 (1955).

(7) M. Blau, W. T. Carnall and J. E. Willard, *ibid.*, **74**, 5762 (1952).

peratures, it seems likely that FeCl_3 exchanges rapidly with liquid hydrogen bromide and thus the catalyst for the addition (and subsequent reactions) is largely FeBr_3 . Evidently the complex, $\text{HBr}\cdot\text{FeBr}_3$, is a more effective reagent than hydrogen bromide in the rate-determining step of the ionic addition.

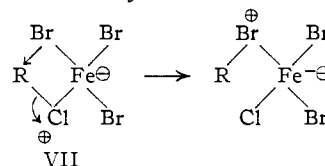
The initially formed addition product II undergoes halogen exchange followed by rearrangement (isomerization). That ferric halide promotes these reactions is clear from the fact that they do not occur in its absence. Presumably the chlorobromide II exchanges halogen with FeBr_3 to form the dibromide III and ferric bromochloride which is reconverted to FeBr_3 by equilibration with the medium.

Halogen exchange reactions of this type have been observed with a variety of electrophilic metal halides, e.g., AlCl_3 ,⁸ AlBr_3 ,⁹⁻¹¹ AlI_3 ,¹⁰ SnCl_4 ,^{6,12} SnBr_4 ,⁹ and GaCl_3 .¹³ It has been suggested¹⁴ that a high boiling by-product obtained from the addition of hydrogen bromide to trichloromethyl-ethylene in the presence of ferric halide is due to halogen exchange.

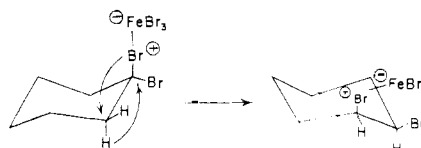
There are also a number of examples of rearrangements of the type encountered in the present work. Isomeric rearrangements of alkyl halides in the presence of AlCl_3 ,^{8b,15} and AlBr_3 ,^{10,16,17} have been observed. The rearrangement of 2-chlorocyclohexyl phenyl ketone to 4-chlorocyclohexyl phenyl ketone by AlCl_3 ^{15c} is apparently similar to the conversion of dibromocyclohexanes to VI. The observation that exchange is more rapid than rearrangement parallels the observation of Sixma and co-workers that ethyl bromide exchanges halogen with AlBr_3 ,¹¹ more rapidly than ethyl β -C¹⁴ bromide is isomerized under similar conditions.¹⁷

From available information concerning isomerization and halogen exchange of alkyl halides in the presence of electrophilic metal halides,^{10,12,13} it seems likely that in the present case a complex (addition product) between the alkyl halide and FeCl_3 is the reactant for both processes. Since dissociated carbonium ions apparently are not involved in the rearrangement, which is much slower than exchange, it follows that such intermediates are unlikely in the exchange reaction. The present results appear to be consistent with the intra-

molecular process illustrated by VII which is similar to a mechanism suggested for the halogen exchange between methyl bromide and GaCl_3 .¹³ In systems where R corresponds to a stable carbonium ion, exchange probably involves ionization of the complex to form the carbonium ion followed by recombination.¹³ It is noteworthy that it has been shown that neither halogen exchange reactions⁶ nor isomerizations^{15b} of this type involve elimination followed by addition.



Perhaps the most significant observation of the present work is that the 1,1-dibromide III is evidently converted exclusively to *cis*-1,2-bromocyclohexane (IV). This clearly rules out any mechanism involving the 2-bromocyclohexylcarbonium ion for this intermediate would give rise to the *trans*-1,2-isomer.¹⁹ The observed stereochemical result of this rearrangement is consistent with a previously suggested¹⁰ mechanism for the isomerization of propyl bromide to isopropyl bromide in the presence of AlBr_3 . This mechanism amounts to an isomeric Wagner-Meerwein rearrangement of the alkyl halide-metal halide complex and is summarized for the present system by VIII. As shown in this illustration, the usual stereochemical observation for such a rearrangement, i.e., inversion of the carbon atoms from which and to which migration occurs,²⁰ indeed results in the conversion of III to IV. The bromine atom and hydrogen atom which migrate are both axial in the reactant and product. Such mechanistic details as (1) which of the four bromine atoms attached to iron in VII becomes attached to C₂ and (2) whether or not intermediates are involved in the rearrangement, e.g., an internal ion-pair intermediate,²¹ are not known.



VIII

Rearrangement of the *cis*-1,2-dibromide IV by the process illustrated by VIII would give *cis*-1,3-dibromocyclohexane. As indicated above, the configuration of V was not established. Details

(18) See J. W. Bayles, A. G. Evans and J. R. Jones, *J. Chem. Soc.*, 1020 (1957), for examples of ionization reactions of this type.

(19) See S. Winstein, *THIS JOURNAL*, **64**, 2792 (1942). The present data do not rule out the possibility that *trans*-1,2-dibromocyclohexane is an intermediate but relatively reactive so that its steady-state concentration is low. However, if it is an important intermediate in the stepwise conversion of III to VI, the *cis*-1,2-dibromide IV apparently must be a precursor and the first intermediate. It appears to be inconsistent that *trans*-1,2-dibromocyclohexane could be a precursor for the less stable *cis*-1,2-dibromide and also have a much lower steady-state concentration.

(20) P. D. Bartlett in H. Gilman, "Organic Chemistry, an Advanced Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, Chap. I.

(21) S. Winstein, *et al.*, *THIS JOURNAL*, **78**, 328 (1956).

(8) (a) C. H. Wallace and J. E. Willard, *THIS JOURNAL*, **72**, 5275 (1950); M. Blau and J. E. Willard, *ibid.*, **73**, 442 (1951); (b) G. W. Pearce and S. Krause, *ibid.*, **79**, 271 (1957).

(9) F. Fairbrother, *J. Chem. Soc.*, 293 (1941).

(10) H. C. Brown and W. J. Wallace, *THIS JOURNAL*, **75**, 6279 (1953).

(11) F. L. J. Sixma, H. Hendriks and D. Holtzapffel, *Rec. trav. chim.*, **75**, 127 (1956).

(12) R. A. Howald and J. E. Willard, *THIS JOURNAL*, **78**, 6217 (1956).

(13) H. C. Brown, L. P. Eddy and R. Wong, *ibid.*, **75**, 6275 (1953).

(14) M. S. Kharasch, E. H. Rossin and E. K. Fields, *ibid.*, **63**, 2558 (1941).

(15) (a) J. D. Roberts, R. E. McMahon and J. S. Hine, *ibid.*, **72**, 4237 (1950); R. M. Roberts, G. A. Ropp and O. K. Neville, *ibid.*, **77**, 1764 (1955); (b) L. M. Nash, T. I. Taylor and W. E. Doering, *ibid.*, **71**, 1516 (1949); (c) C. L. Stevens and E. Farkas, *ibid.*, **75**, 3306 (1953).

(16) P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1531 (1944).

(17) F. L. J. Sixma and H. Hendriks, *Rec. trav. chim.*, **75**, 169 (1956).

TABLE III
 PHYSICAL PROPERTIES OF DIHALOCYCLOHEXANES

Cyclohexane derivative	B.p.		n_D^{25}	d_4^{25}	M.p., °C.
	°C.	Mm.			
1,1-Dibromo-	76-77	8.5	1.5405	1.746	-33 to -29.5
1-Bromo-1-chloro-	77.5	17	1.5093	1.454	-43 to -42
<i>cis</i> -1,2-Dibromo-	104	9	1.5523	1.803	10.0 to 10.5
<i>trans</i> -1,2-Dibromo-	90.1-90.8	9	1.5507	1.784	-4.5 to -2.5
<i>cis</i> -1-Bromo-2-chloro-	87.5-88	7	1.5238	1.508	-7.5 to -5.5
<i>trans</i> -1-Bromo-2-chloro-	76.5-77	9	1.5173	1.479	-19.5 to -18

of the conversion of V to VI are not clear. It is possible that the FeBr_3 complex of *cis*-1,3-dibromocyclohexane ionizes to give (1) the corresponding cation which rearranges to the 4-bromocyclohexyl cation which may be bridged²² as illustrated by IX or (2) the bridged ion IX directly. Reaction of bromide ion or its equivalent with 4-bromocyclohexylcarbonium ion under reversible conditions would give VI whether the cation is bridged or not.



Experimental

Materials.—1-Chlorocyclohexene, b.p. 140-142°, n_D^{25} 1.4772, and 1,1-dichlorocyclohexane, n_D^{25} 1.4788, d_4^{25} 1.154, were prepared by the method of Carroll, *et al.*²³ 1-Bromocyclohexene, b.p. 62-63° (20 mm.), n_D^{25} 1.5152, was prepared from *trans*-1,2-dibromocyclohexane in yields of about 5%.³ This material also was prepared by dehydrobromination of 1,1-dibromocyclohexane (see below). The physical properties of authentic samples of 1,1- and 1,2-dihalocyclohexanes required for comparison of physical properties and infrared spectra with various reaction products are given in Table III. The preparations of these compounds have been described in earlier papers.^{3,24} All of these samples are believed to be homogeneous and structural assignments are consistent with (a) method of synthesis, (b) relative physical properties, (c) dipole moments,²⁵ (d) relative reactivities²⁴ and (e) various chemical reactions, *viz.*, products of elimination.²⁴

Authentic *trans*-1,4-dibromocyclohexane, m.p. 112-114° (lit.²⁶ 112°), was prepared from 1,4-dihydroxycyclohexane²⁷ and hydrobromic acid.²⁸

"1,3-Dibromocyclohexane" was obtained as follows: Phosphorus tribromide (173 g.) was added dropwise to 56 g. 1,3-dihydroxycyclohexane.²³ The reaction mixture was stirred during the addition. After cooling, the reaction mixture was poured on ice and extracted with ether. After drying (CaCl_2), the ether was removed by distillation and the residue was fractionated. The main fraction, 75.6 g. (65%), b.p. 91-98° (9 mm.), was carefully fractionated with a tantalum wire spiral column.²⁹ Three grams of *trans*-1,4-dibromocyclohexane, m.p. 110-114°, was isolated from the forerun. The fraction believed to consist largely of 1,3-dibromocyclohexane³⁰ had b.p. 93.5-95.0° (6 mm.), n_D^{25}

(22) See D. S. Noyce and B. R. Thomas, *THIS JOURNAL*, **79**, 755 (1957).

(23) B. Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, *ibid.*, **73**, 5382 (1951).

(24) H. L. Goering and H. H. Espy, *ibid.*, **78**, 1454 (1956); **77**, 5023 (1955).

(25) P. Bender, D. L. Flowers and H. L. Goering, *ibid.*, **77**, 3463 (1955).

(26) K. Kozima and T. Yoshino, *ibid.*, **75**, 166 (1953).

(27) R. C. Oldberg, H. Pines and V. N. Ipatieff, *ibid.*, **66**, 1096 (1944).

(28) M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 2103 (1950).

(29) That fractionation with this column does not isomerize dibromocyclohexanes is clearly shown by the fact that the dihalides listed in Table III were fractionated without rearrangement.

(30) This product probably is not homogeneous. The infrared spectrum indicated that the product contains some *trans*-1,4-dibromocyclohexane.

1.5488, d_4^{25} 1.764, MR 43.63 (calcd. 43.24) (lit.³¹ b.p. 110° (19 mm.), n_D^{25} 1.5430).

Anal. Calcd. for $\text{C}_6\text{H}_{10}\text{Br}_2$: C, 29.78; H, 4.17. Found: C, 30.22; H, 4.12.

Anhydrous ferric chloride and anhydrous hydrogen bromide were obtained from the Allied Chemical and Dye Corporation and the Matheson Co., respectively.

Reaction of 1-Chlorocyclohexene with Hydrogen Bromide in the Presence of Ferric Chloride.—Ten grams of pure 1-chlorocyclohexene and a weighed amount of anhydrous ferric chloride (0.1-2.0 g.) were placed in a 250-ml. Pyrex bomb liner equipped with a gas-inlet tube and exit tube attached to a drying tube. The liner was cooled in liquid air and about 50 g. of anhydrous hydrogen bromide was added. The liner was placed in a bomb and after 24 hr. at room temperature the bomb was vented and the reaction mixture was extracted with three 125-ml. portions of pentane. The pentane solution was washed with water and 10% sodium carbonate solution and dried. The products were isolated by distillation (a three-inch Vigreux column was used for the distillation) at reduced pressure except in the experiments which gave primarily *trans*-1,4-dibromocyclohexane in which case the product was isolated as a solid residue and purified by recrystallization.

Under the above conditions the composition of the product depends on the amount of ferric chloride used. The results of several experiments are given in Table I. The products were identified by comparison of physical properties and infrared spectra with those of authentic samples of dihalocyclohexanes (Table III). All of the experiments listed in Table I were reproducible and several, *viz.*, the ones from which pure compounds can be isolated readily (*e.g.*, expt. 2, 4 and 6), were repeated several times.

With from 0.1 to 0.4 g. of ferric chloride (expt. 1 and 2) the normal ionic addition product 1-bromo-1-chlorocyclohexane was isolated in yields of 69-90%. The infrared spectrum of the product was indistinguishable from that of an authentic sample of 1-bromo-1-chlorocyclohexane. The addition of hydrogen bromide to 1-chlorocyclohexene and 1-bromocyclohexene under these conditions has been described previously.³

The product from expt. 3 (0.6 g. of FeCl_3) had an infrared spectrum that was a composite of the spectra for 1-bromo-1-chlorocyclohexane and 1,1-dibromocyclohexane. From the spectrum (and refractive index) the composition of the product was estimated to be 60% 1,1-dibromocyclohexane and 40% 1-bromo-1-chlorocyclohexane.

Essentially pure 1,1-dibromocyclohexane was isolated in yields of 75-80% when 0.75 g. of ferric chloride was used (expt. 4). The infrared spectrum of the product was indistinguishable from that of an authentic sample. Large amounts of the pure dibromide were prepared by this method. Dehydrobromination gave 1-bromocyclohexene in good yields (see below).

A complex mixture resulted when 1 g. of ferric chloride was used (expt. 5). When 45 g. of material prepared by this method was carefully fractionated with a tantalum wire spiral column,²⁹ these fractions were obtained (Table IV).

The spectrum of fraction 1 was essentially the same as that of 1,1-dibromocyclohexane, the dibromocyclohexane with the lowest boiling point (Table IV). The spectrum of fraction 2 was complex and contained all of the characteristic bands for 1,3- and 1,4-dibromocyclohexane. Fraction 3 was mostly crystalline and the solid material was identified as *trans*-1,4-dibromocyclohexane by its melting point (m.p. 110-113°, no depression when mixed with an authentic sample) and infrared spectrum. The spectrum of frac-

(31) R. Cornubert, A. Rio and P. Senechal, *Bull. soc. chim.*, **46** (1955).

TABLE IV

Fraction	B.p., °C. (8 mm.)	Wt., g.	n_D^{25}
1	71-94	0.9	1.5408
2	94-96	1.4	1.5482
3	96-98	11.5	
4	98-99	7.3	1.5511
5	98.5	15.8	1.5515

tion 4 indicated that this material was largely *cis*-1,2-dibromocyclohexane contaminated with 1,3-dibromocyclohexane and *trans*-1,4-dibromocyclohexane. The bands at 14.65 μ (strong) and 11.9 μ (medium) which are present in the spectrum of *trans*-1,2-dibromocyclohexane but not in the spectra of the other dibromocyclohexanes were conspicuously absent in the spectrum of fraction 4 (and in the spectra of the other fractions). Fraction 5 was found to be essentially pure *cis*-1,2-dibromocyclohexane. Except for weak bands or shoulders at 10.5 (1,3-dibromo- and/or *trans*-1,4-dibromocyclohexane), 12.2, 13.6 and 13.8 μ (1,3-dibromocyclohexane), the spectrum of this fraction was indistinguishable from that of pure *cis*-1,2-dibromocyclohexane. Bands characteristic of *trans*-1,2-dibromocyclohexane, e.g., 10.0 μ (strong), 14.65 μ (strong), etc., were completely absent. It has previously been found³ that 2% of *trans*-1,2-dibromocyclohexane in *cis*-1,2-dibromocyclohexane can be detected by infrared analysis. Thus there is little doubt but that less than 2% of *trans*-1,2-dibromocyclohexane is present in any of the fractions, and there is no evidence that this material was present in any of the fractions.

1-Bromocyclohexene.—In previous work this compound was obtained in low yields from the dehydrobromination of *trans*-1,2-dibromocyclohexane. In the present work it was found that this compound can be prepared far more conveniently from 1-chlorocyclohexene. 1-Chlorocyclohexene was converted to 1,1-dibromocyclohexane as described above (expt. 4) and the latter compound was dehydrobrominated as follows: A mixture of 36.1 g. (0.15 mole) of 1,1-dibromocyclohexane and 50 g. of freshly distilled quinoline was refluxed for 1 hr. After cooling, the reaction mixture was diluted with 150 ml. of water and acidified with concentrated hydrochloric acid. The reaction mixture was extracted with ether. After drying (CaCl₂) the ether was removed by distillation. The residue was distilled and 17.5 g. (73%) of 1-bromocyclohexene, b.p. 44-46° (7 mm.), n_D^{25} 1.5109, was obtained. The infrared spectrum of this material was indistinguishable from that of 1-bromocyclohexene prepared from *trans*-1,2-dibromocyclohexane.³ By this method 1-bromocyclohexene can be prepared from the readily available 1-chlorocyclohexene²³ in yields of 50-60%.

Conversion of 1-Bromocyclohexene and Dihalocyclohexanes to *trans*-1,4-Dibromocyclohexane.—The same procedure as described above for the conversion of 1-chlorocyclohexane to *trans*-1,4-dibromocyclohexane (expt. 6) was used for these experiments. The results of these experiments are summarized in Table II which shows the amount of solid *trans*-1,4-dibromocyclohexane isolated in the various experiments. In experiment 8, 14 g. of liquid product, b.p. 95-98° (7 mm.), n_D^{25} 1.5500, was isolated in addition to the 2.2 g. of *trans*-1,4-dibromocyclohexane, m.p. 110-112°. The liquid fraction was fractionated carefully and the spectra of the various fractions showed that *trans*-1,4-, *cis*-1,2- and 1,3-dibromocyclohexane were present. That only dibromocyclohexanes were present was clearly shown by the chemical composition (carbon-hydrogen analysis) of each fraction. There was no evidence for the presence of *trans*-1,2-dibromocyclohexane. In experiment 14, a liquid product, 11.8 g., b.p. 92-97° (7 mm.), n_D^{25} 1.5490, was obtained together with 5.6 g. of *trans*-1,4-dibromocyclohexane. The liquid fraction had a spectrum essentially the same as that for 1,3-dibromocyclohexane. The chemical composition of the liquid fraction (carbon-hydrogen analysis) corresponded to that for dibromocyclohexane. *trans*-1,4-Dibromocyclohexane was the only product isolated in experiments 9-13.

Infrared Spectra of Dihalocyclohexanes.—Spectra of liquid films were used for comparison of liquid compounds and products. Spectra of 0.4 *M* carbon disulfide solutions were used for identification of the solid product as *trans*-1,4-dibromocyclohexane. The spectra of the dihalocyclohexanes differ sufficiently so that small amounts of any one can be detected in a mixture of dihalocyclohexanes. Several of the dihalides, viz., 1,1-, *trans*-1,2- and 1,3-dibromocyclohexane, have strong characteristic bands that are absent or shifted in the spectra of the other dihalocyclohexanes. Thus the absence of any of these compounds in a mixture readily can be determined. The following bands were found especially useful for identification purposes (bands not present in the spectrum of any other dihalocyclohexane are marked with an asterisk): 1,1-Dibromocyclohexane, 11.35* and 14.20 μ ; 1-bromo-1-chlorocyclohexane, 13.55 and 13.85 μ ; *trans*-1,2-dibromocyclohexane, 10.00, 10.30, 11.60, 11.90 and 14.64* μ ; *cis*-1,2-dibromocyclohexane, 7.70, 8.23, 10.20 and 12.02 μ ; 1,3-dibromocyclohexane, 9.7* and 8.3 μ ; *trans*-1,4-dibromocyclohexane, 8.6, 10.1, 11.3, 11.5, 13.5 and 13.7 μ ; *cis*-1-bromo-2-chlorocyclohexane, 7.70, 9.22, 11.40, 12.02, 13.5, 14.4 and 15.1 μ ; *trans*-1-bromo-2-chlorocyclohexane, 9.98, 10.5, 11.6, 11.9, 13.5, 14.5 and 15.1 μ .

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Base-catalyzed Elimination and Aromatization of a Cyclohexadieneamine and its Methiodide¹

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Isomeric *n*-amylcyclohexadieneamines, prepared by rearrangement of the 2,4,6-trimethylbenzyltrimethylammonium ion and condensation of the resulting *exo*-methylenecyclohexadieneamine with butyllithium, was found to eliminate the carbanion of trimethylamine to form *n*-amylmesitylene with potassium amide in refluxing xylene and with potassium *n*-pentoxide in refluxing *n*-pentanol. A catalytic amount of potassium amide was sufficient for this aromatization. The methiodides of the *n*-amylcyclohexadieneamines underwent aromatization with potassium amide even in liquid ammonia, the carbanion of the tetramethylammonium ion being eliminated.

Recently² aromatic quaternary ammonium ion I was rearranged by sodium amide in liquid ammonia to *exo*-methylenecyclohexadieneamine II which was condensed with butyllithium in ether to form a mixture of isomeric *n*-amylcyclohexadieneamines IVa

and IVb (equation 1). This condensation involved the attack of the potential butyl carbanion of the reagent at the *exo*-methylene group of II to form yellow *n*-amylcyclohexadienyl carbanion III which was hydrolyzed.

The mixture of isomeric alicyclic amines IVa and IVb was rearomatized by means of butyllithium in refluxing ether to produce *n*-amylmesitylene (V).

(1) Supported by the National Science Foundation.

(2) C. R. Hauser and D. N. Van Eenam, *THIS JOURNAL*, **78**, 5512 (1957).