pounds in the two solvents shows, as predicted by Kozima, *et al.*,[2] that there is no apparent solvent effect. The low value for the *cis*-1,2-dibromide is attributed to experimental error, since the pertinent data were in this case the least precise.

It is interesting to note that the observed dipole moment of 2.46 *D* for the 1,1-dihalocyclohexanes corresponds to an apparent carbon–halogen bond moment of 2.17 *D* (assuming a tetrahedral carbon bond arrangement), which is somewhat larger than the corresponding bond moment of 1.9 *D* for the 1,2-dihalides. Evidently the contributions of the cyclohexane carbon–carbon bond moments induced by the halogen atoms (inductive effect) to the apparent carbon-halogen bond moment is larger for 1,1- than for 1,2-dihalocyclohexanes. This is to be expected since the inductive effects of the halogens complement each other in the 1,1-dihalocyclohexanes whereas there is cancellation of inductive effects in the C_1–C_2 bond in the 1,2-dihalides. The contributions of inductive effects to the dipole moment of cyclohexyl chloride (or bromide) should be at least as large as they are to the apparent carbon–halogen moments in 1,1-dihalocyclohexanes. Thus the apparent carbon–halogen moment of 2.17 *D* in 1,1-dihalocyclohexanes would be expected to be a lower limit for the dipole moment of cyclohexyl chloride (or bromide). Because of discrepancies in the values reported for the dipole moment of cyclohexyl chloride,[16,17] 2.07 to 2.30 *D*, and because the lower value, 2.07 *D*, was incompatible with the present results, the dipole moment of this compound was redetermined; a value of 2.24 *D* was obtained.

Iodide ion-promoted dehalogenation and solvolytic reactivities of the 1,2-dihalocyclohexanes here reported will be described in a later paper.

(16) J. W. Williams, THIS JOURNAL, **52**, 1831, 1838 (1930).

(17) O. Hassel and E. Naeshagen, *ibid.*, **19**, 434 (1932).

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Stereochemistry of Radical Additions. II. The Radical and Ionic Addition of Hydrogen Bromide to 1-Bromocyclohexene and 1-Chlorocyclohexene[1,2]

BY HARLAN L. GOERING AND LESLIE L. SIMS

RECEIVED JANUARY 7, 1955

Radical additions of hydrogen bromide to 1-bromo- and 1-chlorocyclohexene in pentane give the corresponding *cis*-1,2-dihalocyclohexanes (*trans*-addition) containing less than 1% of the *trans*- isomers. In anhydrous ether radical additions could not be promoted by ultraviolet irradiation and from these reactions only the 1,1-dihalocyclohexanes (products of ionic addition) were isolated. Radical addition is promoted by ultraviolet light in a solvent consisting of 31 mole per cent. ether in pentane and in this solvent the addition appears to be as stereospecific (*trans*-addition) as it is in pentane. The radical addition of hydrogen bromide (initiated by benzoyl peroxide) was also investigated in a homogeneous equimolar mixture of hydrogen chloride and pentane and in this medium the addition is also as stereospecific as it is in pure pentane. Ionic additions of hydrogen bromide to 1-bromo- and 1-chlorocyclohexene give 1,1-dibromocyclohexane and 1-bromo-1-chlorocyclohexane, respectively.

Introduction

In the preceding paper[1] in this series evidence was presented indicating a stereospecific *trans*-addition is involved in the radical addition of hydrogen bromide to 1-methylcyclohexene and 1-bromocyclohexene (Ia). *cis*-1,2-Dibromocyclohexane (IIa), the *trans*-addition product, was the only product isolated from the radical addition of hydrogen bromide to Ia. With 1-methylcyclohexene the radical addition could not be isolated completely from ionic addition and mixtures of 1-bromo-1-methylcyclohexane (the ionic-addition product) and *cis*-1-bromo-2-methylcyclohexane (the *trans*-addition product of radical addition) were obtained. We have extended our studies of the stereochemistry of radical additions and this paper describes radical and ionic additions of hydrogen bromide to 1-bromocyclohexene (Ia) and 1-chlorocyclohexene (Ib) under various conditions.

Radical Additions

The radical addition of hydrogen bromide to 1-chlorocyclohexene (Ib) proceeds rapidly in pentane at 0 and −20° when initiated with ultraviolet light and gives *cis*-1-bromo-2-chlorocyclohexane (IIb) (the *trans*-addition product). It is clear that this is a radical addition since addition does not occur in the absence of irradiation. The observed orientation also indicates that a radical addition is involved. The structure of IIb was established by (1) comparison of its physical properties and infrared spectrum with those of *trans*-1-bromo-2-chlorocyclohexane (IIIb) and 1-bromo-1-chlorocyclohexane (IVb), (2) dehydrobromination (*trans*-elimination),[3] by refluxing with sodium ethoxide in ethanol, to Ib and (3) dipole moment measurements.[4] The *trans*-1-bromo-2-chlorocyclohexane (IIIb) used for comparison was prepared from cyclohexane, N-bromosuccinimide and hydrogen chloride according to a standard procedure for preparing vicinal bromochlorides.[5] This compound, when refluxed with sodium ethoxide in ethanol, was converted to 3-ethoxycyclohexene which was identified by comparison with an authentic sample prepared by the ethanolysis of 3-bromocyclohexene.

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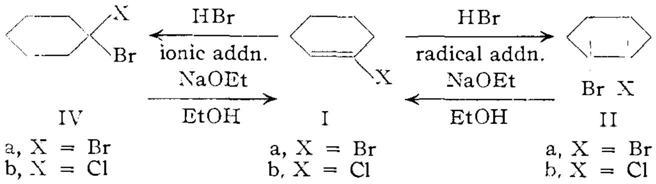
[1] Paper No. 1, H. L. Goering, P. I. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952).

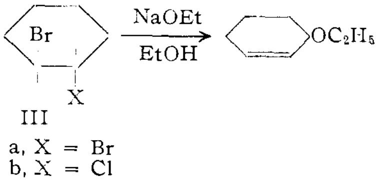
[2] This work was supported in part by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command and in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

[3] S. J. Cristol, THIS JOURNAL, **69**, 338 (1947).

[4] P. Bender, D. L. Flowers and H. L. Goering, *ibid.*, **77**, 3463 (1955). See also W. Kwestroo, F. A. Meijer and E. Havinga, *Rec. trav. chim.*, **73**, 717 (1954).

[5] J. B. Ziegler and A. C. Shabica, THIS JOURNAL, **74**, 4891 (1952).





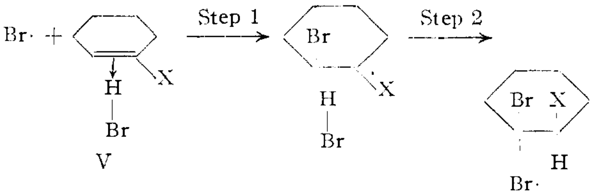
The infrared spectra of crude radical-addition products (IIb), m.p. −11° to −8°, isolated from additions at 0 and −20° in such a way as to avoid fractionation of the possible isomers, were indistinguishable from that of pure IIb, m.p. −7.5 to −5.5° (purified to constant physical properties by recrystallization and fractionation), and did not have detectable bands characteristic of *trans*-1-bromo-2-chlorocyclohexane. In order to determine if any of the *cis*-adduct, IIIb, is formed, the crude addition product was fractionated with an efficient column. Under the conditions of the fractionation (8 mm.) the *trans*-isomer (*cis*-adduct), IIIb, boils about 10° lower than the *cis*-isomer (IIb). The first fraction (10% of the total amount) was found to contain 3 ± 1% of the *cis*-adduct, IIIb, by infrared analysis. The second (3% of the total amount) and subsequent fractions did not contain detectable amounts of IIIb indicating that all of it was present in the first fraction. The amount of IIIb in the first fraction corresponds to 0.3% of the product indicating that the radical addition is 99.7% *trans* (to give IIb) and 0.3% *cis* (to give IIIb).

It has been been shown previously[1] that the radical addition of hydrogen bromide to 1-bromocyclohexene (Ia) gives the *trans*-adduct, *cis*-1,2-dibromocyclohexane (IIa). In the present work we have re-examined the product of this reaction (carried out in pentane at 0 and −20°) to determine if any *trans*-1,2-dibromocyclohexane (IIIa) (the *cis*-adduct) is formed. The addition product, m.p. 6–8°, isolated in such a way as to avoid fractionation had an infrared spectrum indistinguishable from that of pure IIa, m.p. 10.0–10.5°. When the crude product was fractionated the first fraction (13% of the total amount) contained 4 ± 1% of the *cis*-addition product, IIIa. As in the case of the chlorobromides the *trans*-isomer (IIIa) boils about 10° lower than the *cis*-isomer (IIa) and was concentrated in the first fraction. From the amount of IIIa in the first fraction it follows that the addition product consists of 99.5% IIa (*trans*-addition) and 0.5% IIIa (*cis*-addition).

The above results confirm our earlier observation[1] that *trans*-addition is preferred and show that *trans*-addition is over 100 times faster than *cis*-addition even though in the systems that we have worked with the *trans*-adducts (*cis*-1,2-disubstituted cyclohexanes) are thermodynamically less stable than the *cis*-adducts (*trans*-1,2-disubstituted cyclohexanes).[6]

A possible explanation for the stereospecific *trans*-addition is that the substrate (I) is "π complexed"[7] (V) with excess hydrogen bromide and the chain-carrying bromine atom adds to the double bond from the side opposite to the complexed hydrogen bromide molecule to form the *trans*-adduct. This process may be visualized as a two-step process as illustrated in Chart I or as a concerted process in which addition (step 1) and transfer (step 2) are simultaneous.

CHART I



It seems likely that under the conditions of our previous experiments[1] and the ones described above (*i.e.*, excess hydrogen bromide in pentane) the substrate (I) may well be complexed to a considerable extent. It has been shown[7] that hydrogen chloride–olefin "π complexes" exist under similar conditions and there is evidence that indicates hydrogen bromide is more effective than hydrogen chloride for forming similar complexes.[8] In addition to accounting for the stereochemistry, this modification of the mechanism suggested by Kharasch and co-workers[9] also offers a possible explanation for the efficient transfer step in radical additions involving hydrogen bromide, as indicated by the long chains and the apparently low tendency for telomer formation.[10]

Two experiments were carried out to test the hypothesis illustrated in Chart I. In the first experiment the ultraviolet light promoted radical addition of hydrogen bromide (0.24 mole) to Ib (0.085 mole) was investigated in pentane containing 0.68 mole of anhydrous ether. Since hydrogen bromide would be expected to complex more readily with ethers than with Ib,[8] it seems likely that under these conditions Ib is not appreciably complexed with hydrogen bromide. The radical addition product, isolated in such a way as to avoid fractionation, had an infrared spectrum indistinguishable from that of pure IIb, indicating that the addition is as stereospecific as when ether is not present.

In the second experiment the benzoyl peroxide initiated radical addition of hydrogen bromide (0.1 mole) to Ib (0.072 mole) was carried out in a homogeneous mixture of 1 mole of pentane and 1 mole of hydrogen chloride. Although hydrogen bromide probably has a greater tendency than hydrogen chloride to complex with olefins, it seems likely that under the present conditions if Ib is indeed complexed at all it will for the most part be complexed with hydrogen chloride which is present in largest

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(6) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(7) H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

(8) A. J. Weith, M. E. Hobbs and P. M. Gross, *ibid.*, **70**, 805 (1948).

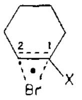
(9) M. S. Kharasch, H. Engelmann and F. R. Mayo, *J. Org. Chem.*, **2**, 288 (1937). See also D. H. Hey and W. A. Waters, *Chem. Rev.*, **21**, 169 (1937).

(10) (a) F. R. Mayo and C. Walling, *ibid.*, **27**, 351 (1940); (b) see also R. N. Haszeldine and B. R. Steel, *J. Chem. Soc.*, 3747 (1954).

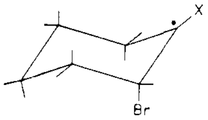
amounts. Since hydrogen chloride cannot in general undergo the transfer step in a radical addition,[10a,11] the addition of a bromine atom to a Ib–hydrogen chloride "π complex" could not be followed by a rapid transfer reaction of the type depicted in Chart I. The product isolated from this experiment was collected in two fractions. The infrared spectrum of the more volatile fraction (7% of the product) indicated that it contained primarily 1-bromo-1-chlorocyclohexane (IVb) together with lesser amounts of 1,1-dichlorocyclohexane and IIb. There were no bands characteristic of IIIb (the *cis*-radical adduct). The spectrum of the second fraction (93% of the product) was indistinguishable from that of pure IIb. The formation of the *gem*-dihalides indicates that radical addition was not completely isolated from ionic addition. However, it appears that the stereospecificity of the radical addition is unaffected by the presence of large amounts of hydrogen chloride. The results of this and the above experiment indicate that the formation of a Ib–hydrogen bromide complex prior to addition is not a necessary requirement for stereospecific *trans*-addition.

In the previous paper,[1] VI[12] was suggested as a possible structure for the radical resulting from the first step of the chain process to account for the stereospecific *trans*-addition. If indeed VI is the structure of the intermediate radical, *trans*-addition would be expected since chain transfer (the second step in the chain process) would occur at C_1 from the opposite direction of the bromine bridge.

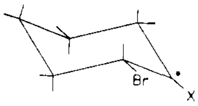
Another possible structure for the intermediate radical which is consistent with the preferred *trans*-addition is the classical structure, VIIa, in which the C_2 bromine occupies an axial position. Scale models show that if the radical has this conformation there is a steric advantage, in the transfer step, for the hydrogen bromide molecule to approach the radical from the side away from the C_2-axial bromine. This explanation for *trans*-addition was previously[1] considered unlikely since it was assumed that the classical radical would exist for the most part in the conformation in which the C_2 bromine occupies an equatorial position (VIIb), and in which there is little or no steric advantage for the approach of the hydrogen bromide molecule so as to lead to *trans*-addition. In view of recent work[13] concerning the relative stabilities of the two chair forms of substituted cyclohexanes and cyclohexanones it appears that our original assumption that VIIb is a more stable conformation than VIIa may not be valid. Although VIIb is sterically less strained than VIIa, the carbon–halogen bonds in VIIb are nearly coplanar (eclipsed) and this form is thus destabilized by electrostatic interactions (carbon–halogen dipole repulsion). Because of the opposing steric and electrostatic interactions it is difficult to assess the relative stabilities of VIIa and VIIb. Even if VIIb is more stable than VIIa the latter conformation may be involved in radical additions. As has been pointed out,[14] it seems likely that in radical additions the chain carrying radical approaches the double bond perpendicular to the plane of the sigma bonds of the ethylenic linkage (*i.e.*, in line with the carbon p_z orbitals). In the present system this would result in the formation of VIIa and if the latter undergoes the transfer step, before being converted to VIIb, *trans*-addition would be expected. It thus appears that either structure VI, or VIIa, for the intermediate radical is consistent with the observed *trans*-addition.



VI



VIIa



VIIb

Ionic Additions

When hydrogen bromide is passed through an ether solution of Ia, 1,1-dibromocyclohexane (IVa) is obtained in good yields. Under similar conditions Ib is converted to 1-bromo-1-chlorocyclohexane (IVb). Evidently the ionic additions are rapid since ultraviolet irradiation during the reaction did not result in the formation of detectable amounts of "abnormal" addition products. It is interesting to note that when pentane is used instead of ether, ionic addition is so slow that the radical addition readily can be isolated. It has previously been shown[15] that ionic additions of hydrogen chloride and hydrogen bromide to cyclohexene and 3-hexene proceed more rapidly in hydrocarbon solvents than in ether. Under the conditions of our experiments the solvent was saturated with hydrogen bromide and the fact that ionic addition was much slower in pentane than in ether is probably due to the much greater solubility of hydrogen bromide in the latter solvent. Ionic additions of hydrogen bromide to Ia and Ib were also carried out in good yields without solvent in the presence of ferric chloride (to promote ionic addition[10a]) and diphenylamine (to inhibit radical addition[10a]).

The structures of the *gem*-dihalides (IV) were established by (1) comparison of physical properties and infrared spectra with those of the corresponding *cis*- and *trans*-1,2-dihalocyclohexanes, (2) dehydrohalogenation to Ia or Ib, (3) hydrolysis to cyclohexanone and (4) dipole moment measurements.[4]

Experimental[16]

Materials.—*trans*-1,2-Dibromocyclohexane was prepared in *ca.* 84% yield by the method of Snyder and Brooks[17] and purified by recrystallization from pentane followed by fractionation with a tantalum wire spiral column. The pure product (constant physical properties) had: b.p. 90.1–92.3° (8–9 mm.), m.p. −4.5 to −2.5°, $n^{25}D$ 1.5507, d^{25}_4 1.784, MRD 43.24 (calcd. 43.24) (lit.[18] b.p. 99.6–99.9° (13 mm.), m.p. −4.5, $n^{25}D$ 1.5507).

1-Bromocyclohexene, b.p. 62–63° (20 mm.), $n^{25}D$ 1.5125, was prepared from *trans*-1,2-dibromocyclohexane in yields

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[11] F. R. Mayo, THIS JOURNAL, **76**, 5392 (1954).

[12] In the first paper (ref. 1) this structure was represented in terms of resonance theory. A similar structure has been considered for the radical resulting from the addition of an iodine atom to a carbon–carbon double bond (ref. 14).

[13] See E. J. Corey, THIS JOURNAL, **75**, 2301 (1953).

[14] R. M. Noyes, R. G. Dickinson and V. Schomaker, *ibid.*, **67**, 1319 (1945).

[15] S. F. O'Connor, L. H. Baldinger, R. R. Vogt and G. F. Hennion, *ibid.*, **61**, 1454 (1939).

[16] Melting points are corrected.

[17] H. R. Snyder and L. A. Brooks, "Organic Syntheses," Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 171.

[18] S. Winstein, THIS JOURNAL, **64**, 2792 (1942).

of *ca.* 5% by the previously described method.[1] 1-Chlorocyclohexene was prepared according to the procedure of Carroll, *et al.*,[19] and purified by fractionation with an efficient glass center-rod column. This material had b.p. 140–142° (739 mm.), n^{25}_D 1.4772 (lit.[19] b.p. 141–142°, n^{25}_D 1.4772).

trans-1-**Bromo-2-chlorocyclohexane.**—A solution of 123 g. (1.5 moles) of cyclohexene and 600 ml. of chloroform was prepared in a flask equipped with a fritted glass gas inlet tube which extended to the bottom of the flask. A slurry of 250 g. (1.4 moles) of N-bromosuccinimide (recrystallized from water) in 300 ml. of chloroform was added in portions as anhydrous hydrogen chloride was passed through the solution. After the addition of the N-bromosuccinimide and hydrogen chloride the solution was filtered to remove the succinimide, washed with water and 10% sodium carbonate solution and dried over magnesium sulfate. The chloroform was removed by distillation and the distilled product (171 g. or 62%) was purified by recrystallization from pentane followed by fractionation. The pure material had: 76.5–77° (9 mm.), m.p. −19.5° to −18°, n^{25}_D 1.5173, d^{25}_4 1.479, *MR*D 40.40 (calcd. 40.34) (lit.[20] b.p. 94° (17 mm.), n^{20}_D 1.5226, d^{20}_4 1.514).

Radical Addition of Hydrogen Bromide to 1-Chlorocyclohexene. (A) (In Pentane).—The radical additions of hydrogen bromide to 1-chlorocyclohexene in purified pentane were promoted by ultraviolet irradiation using the procedure and apparatus described in the first paper in this series (method B).[1] In the present work about 10 g. (0.085 mole) of chlorocyclohexene in 265 g. (3.7 moles) of pentane were used for each experiment. The temperatures at which the additions were carried out were maintained by placing the quartz reaction flask in either an ice-bath (0°) or Dry Ice–carbon tetrachloride bath (−20°). A reaction time of two hours was used for the reaction at both temperatures. After removal of the excess hydrogen bromide by washing with water and 10% sodium carbonate, the products were isolated in yields of from 84–88% by distillation of the dried pentane solutions. The crude product, isolated by distillation in such a way as to avoid fractionation, had b.p. 91–97° (10 mm.), m.p. −11° to −8°. This material was purified by recrystallization from pure pentane (1 g. of solvent per g. of material) followed by fractionation. Pure *cis*-1-bromo-2-chlorocyclohexane obtained in this way had: m.p. −7.5° to −5.5°, b.p. 87.5–88° (7 mm.), n^{25}_D 1.5238, d^{25}_4 1.508, *MR*D 40.03 (calcd. 40.34). These properties were not changed by additional recrystallizations and fractionations indicating that the material was homogeneous.

Anal. Calcd. for $C_6H_{10}BrCl$: C, 36.48; H, 5.10. Found: C, 36.67; H, 5.08.

The infrared spectra of the crude products, m.p. −11° to −8°, from additions at 0 and −20°, were indistinguishable from that of the purified material, m.p. −7.5° to −5.5°.

The crude addition product, 24.3 g., was fractionated at 8 mm. with an efficient column (rated at > 50 plates at atmospheric pressure). Under these conditions *trans*-1-bromo-2-chlorocyclohexane boils about 10° lower than the *cis*-isomer and if the *trans*-isomer is present it should be concentrated in the early fractions. The first fraction, 2.5 g. (10.3% of the total amount), had a spectrum differing slightly from that of the pure *cis*-isomer. Comparison of this spectrum with spectra of synthetic binary mixtures consisting of 3 and 6% *trans*-1-bromo-2-chlorocyclohexane in the *cis*-dihalide indicated that the first fraction contained 3 ± 1% *trans*-1-bromo-2-chlorocyclohexane. The infrared spectrum of the second fraction, 0.8 g., was indistinguishable from that of the pure *cis*-dihalide indicating that essentially all of the *trans*-isomer was in the first fraction. From the amount of *trans*-isomer in the first fraction, 3 ± 1%, it can be determined that the crude product contains 0.3 ± 0.1% of the *trans*-isomer.

B. (In Ether).—When the addition was carried out in anhydrous ether under the conditions described above 1-bromo-1-chlorocyclohexane was obtained instead of the 1,2-dihalide (see ionic additions below). The adduct corresponding to radical addition could not be obtained in this solvent.

C. (In Ether–Pentane Mixture).—A solution of 10 g. (0.085 mole) of 1-chlorocyclohexene in 50 g. (0.68 mole) of diethyl ether and 110 g. (1.5 moles) of purified pentane was cooled to 0° and 20 g. (0.25 mole) of gaseous anhydrous hydrogen bromide was dissolved in the solution. The stirred solution was irradiated for 12 hours at room temperature. The solution was washed with water and 10% sodium carbonate and dried over calcium chloride. Fractionation of the solution with a Vigreux column gave 3.7 g. (37% recovery) of 1-chlorocyclohexene, b.p. 55–56° (37 mm.), n^{25}_D 1.4784, and 6.2 g. (36%) of *cis*-1-bromo-2-chlorocyclohexene, b.p. 103–108° (20 mm.), n^{25}_D 1.5241. The infrared spectrum of the latter did not show any indication of the presence of the *trans*-isomer.

D. (In Pentane–Hydrogen Chloride Mixture).—A solution of 8.4 g. (0.072 mole) of 1-chlorocyclohexene in 72 g. (1 mole) of pentane was prepared in a 250-ml. centrifuge bottle containing 0.5 g. (0.002 mole) of benzoyl peroxide. The centrifuge bottle was immersed in liquid air and 36 g. (1 mole) of anhydrous hydrogen chloride and 10 g. (0.12 mole) of anhydrous hydrogen bromide were added. The bottle was placed in a bomb and heated to 85° for two days. After cooling, the bomb was vented and the solution was washed with water and 10% sodium carbonate and dried over calcium chloride. The pentane solution was fractionated with a tantalum wire spiral column. After removal of the pentane the following two fractions were collected: 1, b.p. 72–87° (7 mm.), n^{25}_D 1.4948, 0.8 g. (9%); 2, b.p. 87–90° (7 mm.), n^{25}_D 1.5238, 10.5 g. (73%).

The forerun (fraction 1) had an infrared spectrum corresponding to 1-bromo-1-chlorocyclohexane containing small amounts of *cis*-1-bromo-2-chlorocyclohexane and 1,1-dichlorocyclohexane. The infrared spectrum of fraction 2 was indistinguishable from that of pure *cis*-1-bromo-2-chlorocyclohexane. None of the fractions had spectra with bands at 11.88, 11.59, 9.98, 9.67 or 8.42 μ (bands present in the spectrum of the *trans*-1,2-isomer but of lower intensity or absent in the spectrum of the *cis*-1,2- or 1,1-isomer).

The mixture of pentane and hydrogen chloride used as the solvent in this experiment exists as a single phase at room temperature. This was demonstrated by collecting 1.0 g. of pentane and 0.50 g. of anhydrous hydrogen chloride in a liquid air-cooled receiver on a high-vacuum line. The receiver was sealed and when warmed to room temperature a single-phase solution resulted. The volume of this solution was qualitatively the sum of the volumes of the liquid components under the same conditions.

Radical Addition of Hydrogen Bromide to 1-Bromocyclohexene. (A) (In Pentane).—The same procedure was used for this addition as for the addition to 1-chlorocyclohexene. The adduct, m.p. 6–8°, b.p. 111–114° (11 mm.), was obtained in yields of 76–81%. After purification by the method described for the chlorobromide, pure *cis*-1,2-dibromocyclohexane,[1] m.p. 10.0–10.5°, b.p. 103.8–104.1° (9 mm.), n^{25}_D 1.5523, d^{25}_4 1.804, *MR*D 42.89 (calcd. 43.24), was obtained. The infrared spectra of the crude products, m.p. 6–8°, obtained from the additions at 0 and −20° were indistinguishable from that of the purified material, m.p. 10.0–10.5°.

As in the case of the chlorobromides the boiling points of the *cis*- and *trans*-isomers differ by about 10° at 8 mm. and by careful fractionation of 25.3 g. of the crude product, m.p. 6–8°, the more volatile *trans*-isomer was concentrated in the first fraction (3.2 g.). By comparing the spectrum of this material with those of synthetic mixtures, it was determined that the first fraction contained 4 ± 1% *trans*-1,2-dibromocyclohexane. The crude products thus contained about 0.5 ± 0.1% of the *trans*-isomer.

(B) (In Anhydrous Ether).—Under the above conditions the reaction in anhydrous ether gave only 1,1-dibromocyclohexane (see ionic additions) and there was no indication of the formation of the radical adduct (*cis*-1,2-dibromide).

Dehydrohalogenation of 1,1- and 1,2-Dihalocyclohexanes. (A) (*cis*-1-Bromo-2-chlorocyclohexane).—A solution of 6.00 g. (0.03 mole) of *cis*-1-bromo-2-chlorocyclohexane and 0.075 mole of sodium ethoxide in 40 ml. of absolute ethanol was refluxed for 3.5 hours. The solution was diluted with an equal volume of water and extracted with several portions of ether. The combined ether extracts were dried (calcium chloride) and distilled through a short Vigreux column. After removal of the ether by distillation, 2.26 g. (64%) of 1-chlorocyclohexene, b.p. 139–142° (734 mm.), n^{25}_D 1.4790, was obtained which was identified by its physical properties and infrared spectrum.

(B) (*trans*-1-Bromo-2-chlorocyclohexane).—Under the conditions described above, 6.00 g. (0.03 mole) of *trans*-1-

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[19] B. Carroll, *et al.*, THIS JOURNAL, **73**, 5382 (1951).

[20] M. Mousseron, R. Granger and J. Valette, *Bull. soc. chim.*, 244 (1946).

bromo-2-chlorocyclohexane was converted to 3.0 g. (80%) of 3-ethoxycyclohexene, b.p. 80–82° (62 mm.), $n^{25}D$ 1.4511.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.25; H, 11.48.

For identification purposes an authentic sample of 3-ethoxycyclohexene was prepared by stirring a solution of 3-bromocyclohexene,[21] b.p. 76–83° (41 mm.), $n^{25}D$ 1.5221 (lit.[22] b.p. 80° (35 mm.), $n^{25}D$ 1.5230) in absolute ethanol containing an equivalent of sodium ethoxide at room temperature for 12 hours. The ethanol solution was diluted with an equal volume of water and extracted with ether. Fractionation of the dried ether extracts gave a 45% yield of 3-ethoxycyclohexene, b.p. 69–70° (40 mm.), $n^{25}D$ 1.4513. The infrared spectrum of this material was indistinguishable from that of the dehydrobromination product of *trans*-1-bromo-2-chlorocyclohexane.

(C) (**1,1-Dibromocyclohexane**).—When 7.0 g. (0.029 mole) of 1,1-dibromocyclohexane was dehydrobrominated by refluxing with 0.056 mole of sodium ethoxide in 50 ml. of absolute ethanol for 1 hour, 3.88 g. (83%) of 1-bromocyclohexene (identified by its infrared spectrum), b.p. 67–69° (26 mm.), $n^{25}D$ 1.5105, was obtained.

(D) (**1-Bromo-1-chlorocyclohexane**).—Under the above conditions (using a reflux period of 12 hr.) 5.62 g. of 1-bromo-1-chlorocyclohexane was converted to 2.20 g. (69%) of 1-chlorocyclohexene, b.p. 137–140° (740 mm.), $n^{25}D$ 1.4791. The infrared spectrum of this material was indistinguishable from that of pure 1-chlorocyclohexene and did not have bands at 13.98, 10.09 μ (bands present in the spectrum of 1-bromo but not in that of 1-chlorocyclohexene).

Methods of Ionic Addition of Hydrogen Bromide to 1-Bromocyclohexene and 1-Chlorocyclohexene. Method A.—About 0.1 mole of halocyclohexene and 10 g. (0.12 mole) of anhydrous hydrogen bromide were distilled into separate liquid air-cooled receivers containing phosphorus pentoxide on a high-vacuum line. The system was evacuated to $<10^{-4}$ mm. for three hours after which first the halocyclohexene and then the hydrogen bromide were distilled into a third receiver (cooled with liquid air) containing 0.1 g. of anhydrous ferric chloride (Allied Chemical and Dye Corp., "Technical Grade") and 0.1 g. of diphenylamine. The reaction receiver was sealed, removed from the system, shielded with an iron pipe, and allowed to stand at room temperature for 24 hours during which time it was shaken occasionally. The products were isolated as follows: The reaction tube was cooled in liquid air, opened, and the product was dissolved in ether. After shaking with water and 10% sodium carbonate the ether solution was dried (calcium chloride) and fractionated at reduced pressure.

Method B.—About 0.1 mole of halocyclohexene, 0.3 g. of diphenylamine and 0.2 g. of anhydrous ferric chloride were placed in a 250-ml. glass bomb liner. The liner was cooled in liquid air and about 21 g. of anhydrous hydrogen bromide was added. The liner was placed in a bomb at room temperature for 24 hours after which the bomb was vented and the reaction mixture extracted with three 125-ml. portions of pentane. The pentane solution was shaken with water and 10% sodium carbonate and dried. The products were isolated by distillation at reduced pressure.

Method C.—About 0.1 mole of halocyclohexene was dissolved in 200 ml. of anhydrous ether in a flask equipped with a condenser and a fritted glass gas inlet tube. The flask was immersed in an ice-bath and anhydrous hydrogen bromide was passed through the solution for about 2 hr. after which the reaction mixture was washed with water and 10% sodium carbonate solution and dried over calcium carbonate. The products were isolated by distillation at reduced pressure.

Ionic Addition of Hydrogen Bromide to 1-Bromo- and 1-Chlorocyclohexene. (A) (**1-Bromocyclohexene**).—Using method A, 13.4 g. (0.083 mole) of 1-bromocyclohexene was converted to 15.2 g. (76%) of 1,1-dibromocyclohexane, b.p. 84–89° (13 mm.), $n^{25}D$ 1.5383. After purification by fractionation to constant physical properties this material had: b.p. 48–48.5° (0.9 mm.), m.p. −33 to −29.5°, $n^{25}D$ 1.5405, d^{25}_4 1.746, *MR*D 43.53 (calcd. 43.24).

Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.78; H, 4.17; halogen, 66.0. Found: C, 30.16; H, 4.30; halogen, 66.2.

This material was hydrolyzed to cyclohexanone by refluxing 14.3 g. of dibromocyclohexane with 12 g. of barium carbonate in 100 ml. of water for 12 hr. The hydrolysis product was isolated by extraction with ether and identified by conversion to cyclohexanone 2,4-dinitrophenylhydrazone, m.p. 159–161°. The m.p. of this derivative was not depressed when mixed with an authentic sample of cyclohexanone 2,4-dinitrophenylhydrazone, m.p. 160–162°.

Using method B, 13.0 g. (0.081 mole) of 1-bromocyclohexene was converted to 16.5 g. (84%) of 1,1-dibromocyclohexane, which was identified by its physical properties (b.p. 100–105° (26 mm.), $n^{25}D$ 1.5405) and infrared spectrum.

By method C, 16.5 g. of 1-bromocyclohexene was converted to 20.8 g. (84%) of 1,1-dibromocyclohexane, b.p. 74–81° (7 mm.), $n^{25}D$ 1.5406.

(B) (**1-Chlorocyclohexene**).—By method A, 10 g. (0.085 mole) of 1-chlorocyclohexene was converted to 13.4 g. (79%) of 1-bromo-1-chlorocyclohexane, b.p. 64–70° (10 mm.), $n^{25}D$ 1.5092. After purification by fractionation to constant physical properties this material had: b.p. 77.5° (17 mm.), m.p. −43.5° to −41.5°, $n^{25}D$ 1.5093, d^{25}_4 1.454, *MR*D 40.56 (calcd. 40.34).

Anal. Calcd. for $C_6H_{10}BrCl$: C, 36.48; H, 5.10; halogen, 58.3. Found: C, 36.77; H, 5.18; halogen, 57.7.

By refluxing with aqueous barium carbonate this compound was converted to cyclohexanone in 62% yield which was identified by its physical properties and by conversion to cyclohexanone 2,4-dinitrophenylhydrazone, m.p. 158–160°.

Using method B, 11.0 g. (0.094 mole) of 1-chlorocyclohexene was converted to 15.3 g. (82%) of 1-bromo-1-chlorocyclohexane, b.p. 86–89° (26 mm.), $n^{25}D$ 1.5109. The infrared spectrum of this material was indistinguishable from that of pure 1-bromo-1-chlorocyclohexane.

Method C gave 15.9 g. (79%) 1-bromo-1-chlorocyclohexane, b.p. 96–102° (40 mm.), $n^{25}D$ 1.5092, from 12.0 g. of 1-chlorocyclohexene.

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