procedures were modeled after those of Pines and Wackher.[9] The isomerization was carried out in a sealed glass tube in the following manner. The reaction tube was evacuated and 2 g. (0.0075 mole) of aluminum bromide sublimed in. Water (0.10 g., 0.0055 mole) was distilled into the tube and, after its reaction with the aluminum bromide was complete, the hydrogen bromide was pumped off. 2-Methylbutane-1-C^{14} (10.8 g., 0.15 mole) was distilled into the tube which was then cooled in a liquid nitrogen trap and sealed off *in vacuo*. The tube was allowed to stand at room temperature for 15 hours with occasional shaking. The isopentane was then removed under reduced pressure and, on photochemical bromination, yielded 9.6 g. (45%) of labeled *t*-amyl bromide, b.p. 106°. This material was degraded as before.[3]

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

The Stereochemistry of the Free Radical Addition of Hydrogen Bromide to 1-Bromocyclohexene and 1-Methylcyclohexene

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The addition of hydrogen bromide to 1-bromocyclohexene proceeds rapidly when catalyzed by benzoyl peroxide or ultraviolet light. The addition is apparently a free radical reaction as it does not occur in the presence of inhibitors of "abnormal" addition. The single addition product isolated appears to be the previously unreported *cis*-1,2-dibromocyclohexane. The formation of this product indicates a preferred *trans* addition. The addition of hydrogen bromide to 1-methylcyclohexene proceeds rapidly without catalysts and yields 1-bromo-1-methylcyclohexane. In pentane in the presence of benzoyl peroxide or ultraviolet light normal and abnormal addition products are formed simultaneously. The abnormal addition product is dehydrobrominated to 1-methylcyclohexene indicating that it is *cis*-1-bromo-2-methylcyclohexane. The formation of this isomer indicates that free radical addition in this case is also *trans*.

The "abnormal" addition of hydrogen bromide to carbon–carbon double bonds has been investigated in considerable detail by Kharasch and coworkers[2] and found to involve a radical chain reaction.[3] In order to obtain additional information concerning the nature of free radical additions we have investigated the stereochemistry of the free radical addition of hydrogen bromide to double bonds.

The stereochemistry of this addition can be determined by selecting systems where *cis* and *trans* addition give different products, provided that the ethylenic compound and addition products are not isomerized under the conditions of the reactions. As bromine atoms promote *cis–trans* isomerizations[4] presumably by a reversible addition of a bromine atom to the double bond, it is apparent that open chain ethylenic compounds may be partially or completely isomerized prior to addition. Indeed it has been shown that *cis* to *trans* isomerization of stilbene is much faster than free radical addition of hydrogen bromide.[5] Chlorostilbene[6] and 2-bromobutene[7] are also rapidly isomerized by bromine atoms.

In the present work the stereochemistry of the free radical addition of hydrogen bromide to 1-bromocyclohexene (I) and 1-methylcyclohexene (III) was investigated. With cyclic systems complications due to *cis–trans* isomerization of the double bond are avoided. From earlier work concerning the orientation of the abnormal addition of hydrogen bromide[2] the expected adduct from I would be 1,2-dibromocyclohexane and that from III would be 1-bromo-2-methylcyclohexane. The stereochemistry of the addition can be deduced from the configuration of the addition products.

From available information concerning the orientation of elimination reactions[8] and by assuming *trans* elimination[9] to be required in base-promoted dehydrobrominations *cis*-1,2-dibromocyclohexane should be converted to I by dehydrobromination whereas the *trans* isomer could not yield this product. It has been shown[10] that *trans*-1,2-dibromocyclohexane is primarily converted to cyclohexadiene by dehydrobromination in quinoline although small amounts of I are also formed. By similar reasoning III would be the predominating elimination product of *cis*-1-bromo-2-methylcyclohexane whereas 3-methylcyclohexene would have to be the exclusive product from the *trans* isomer.

The data obtained for the addition of hydrogen bromide to 1-bromocyclohexene are summarized in Table I. The additions were catalyzed by benzoyl peroxide[2] and ultraviolet light[11] and were carried out in purified pentane.

Addition proceeds rapidly when catalyzed by benzyl peroxide or ultraviolet light (expt. 1, 2 and 3), but does not occur in the presence of inhibitors of abnormal addition[2] (expt. 4) or under ionic conditions (expt. 5 and 6). In the last two experiments nearly all of the unchanged I was recovered indicating ionic addition to be extremely slow. These observations indicate that addition proceeds by a radical process exclusively and as ionic addition is not competing, 1,1-dibromocyclohexane presumably is not formed.

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[1] (a) Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. (b) Rohm and Haas Co., Philadelphia, Pennsylvania.

[2] See F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

[3] M. S. Kharasch, H. Engelmann and F. R. Mayo, *J. Org. Chem.*, **2**, 288 (1937).

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., p. 376.

[5] M. S. Kharasch, J. V. Mansfield and F. R. Mayo, THIS JOURNAL, **59**, 1155 (1937).

[6] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

[7] M. Lepingle, *Bull. soc. chim. France*, [4] **39**, 741 (1926).

[8] E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

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

[10] N. Zilinsky and A. Gorski, *Ber.*, **44**, 2314 (1911).

[11] W. E. Vaughan, F. F. Rust and T. W. Evans, *J. Org. Chem.*, **7**, 477 (1942).

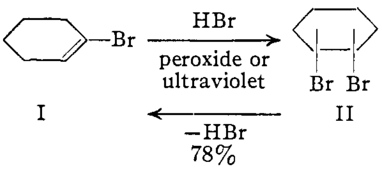
TABLE I

ADDITION OF HYDROGEN BROMIDE TO 1-BROMOCYCLOHEXENE IN PENTANE

Expt.	Mole ratio[a]	Method[b]	Catalyst or reagent	Time, hr.	Temp., °C.	Yield, %	$n^{25}D$
1	11	A	Peroxide	36	25	51	1.5508
2	32	B	Ultraviolet	3.5	35	74	1.5501
3	43	B	Ultraviolet	2	0	86	1.5509
4	11	A	Hydroquinone	48	25	0[c]	
5	0	C	Diphenylamine	2	25	0[c]	
6	0	C	Ferric chloride diphenylamine	2	25	0[c]	

[a] Mole ratio of solvent to I. [b] See Experimental section; method A, reaction carried out in glass lined bomb; method B, reaction carried out in quartz flask equipped with hydrogen bromide bubbler tube and ultraviolet irradiation; method C, reaction carried out in Pyrex flask. [c] No saturated material isolated and most of unchanged olefin recovered.

The addition product isolated in experiments 1, 2 and 3 had the correct analyses for a dibromocyclohexane and melted at 9.7–10.5°. This product, which appears to be homogeneous, depressed the melting point of *trans*-1,2-dibromocyclohexane, m.p. −6°. When dehydrobrominated in refluxing alcoholic potassium hydroxide I was isolated in 78% yield. The product obviously is not *trans*-1,2-dibromocyclohexane and the 1,1-dibromo isomer seems unlikely. By analogy with the dichlorides of cyclohexane[12] the 1,1-isomer would be expected to melt lower than the *trans* 1,2 isomer, which in turn should melt lower than the *cis* 1,2 isomer. Moreover the 1,1-isomer would be expected to hydrolyze readily to cyclohexanone. The addition product was hydrolyzed to a very slight extent when heated with water to 150° for eleven hours. The hydrolysis failed to produce any material that would give a carbonyl test with 2,4-dinitrophenylhydrazine. In view of this evidence we believe the adduct to be the previously unknown[13] *cis*-1,2-dibromocyclohexane (II). The chemistry of this compound is being investigated at the present time.



As *cis*-1,2-dibromocyclohexane is probably thermodynamically less stable than the *trans* 1,2-isomer[14] it appears that II must indeed be the initial product formed. The apparent exclusive formation of this product demonstrates that *trans* addition is preferred.

The results obtained from the addition of hydrogen bromide to 1-methylcyclohexene are summarized in Table II. As expected[2] this compound undergoes ionic addition more rapidly than I. In the presence of benzoyl peroxide (with the exception of experiment 12) or ultraviolet light the "normal" (1-bromo-1-methylcyclohexane) and "abnormal" (1-bromo-2-methylcyclohexane) addition products are formed simultaneously. The composition of the addition product was determined by selective hydrolysis of the tertiary bromide in 80% aqueous acetone at 100°.[15] In order to test this method pure 1-bromo-1-methylcyclohexane (IV) and cyclohexyl bromide were analyzed. These compounds were found to be 100% and 0% tertiary bromide, respectively, verifying the analytical method. In most of the experiments the addition products were analyzed and in every case the product had the correct analysis for methylbromocyclohexane. The yields indicated in Table II correspond to analytically pure methylbromocyclohexane.

TABLE II

ADDITION OF HYDROGEN BROMIDE TO 1-METHYLCYCLOHEXENE IN PENTANE

Expt.	Mole ratio[a]	Method[b]	Catalyst or reagent	Time, hr.	Temp., °C.	Yield,[c] %	*t*-Bromide,[d] %
12	7	C	B.P.[g]	0.2	−80	84.6	100
13	10	C	B.P.	1.0	0	82.2	63.9
13b	10	C	B.P.	4.0	35	89.3	37.6
14	10[e]	C	B.P.	1.5	65	61.2	21.5
15	7	B	Ultraviolet	1.25	35	54.5	22.3
16	7	B	Ultraviolet	4.0	35	24.2	23.4
17	7	B	Ultraviolet	2.0	0	88.0	43.4
18	2[f]	C	Diphenylamine	2.0	25	84.0	100

[a] Mole ratio of solvent to III. [b] See footnote in Table I. [c] Yield corresponds to analytically pure bromo-methylcyclohexanes. [d] Per cent. 1-bromo-1-methylcyclohexane in product. [e] Solvent was hydrocarbon mixture, b.p. 90°. [f] Solvent was acetic acid. [g] Benzoyl peroxides.

It appears that ionic addition gives only IV (experiment 18) and thus the 1-bromo-2-methylcyclohexane must result from the free radical addition. This is also indicated by trends which appear in the table. Thus in the peroxide catalyzed reactions (experiments 12, 13, 13b and 14) the composition of the product varies in a predictable[2] way with increase in temperature. Ionic addition appears to be exclusive at −80°. Increasing the temperature affects the relative rates of ionic and free radical addition so that the latter predominates at temperatures of 35° and over.

As it has been pointed out[15] that the conversion of a secondary to a tertiary bromide may be very facile in the presence of hydrogen bromide we have investigated the stability of the addition product under the conditions of the reaction. A pentane solution of addition product, containing 65.9% tertiary bromide, was refluxed over benzoyl peroxide. The solution was irradiated and dry hydrogen bromide was passed through the solution for 12 hours. The addition product was recovered in 92% yield and contained 66.9% tertiary bromide. In view of these findings we believe the addition products isolated are indeed the initial products formed.

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

(13) See S. Winstein, *ibid.*, **64**, 2792 (1942).

(14) C. W. Beckett, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2488 (1947).

(15) C. Walling, M. S. Kharasch and F. R. Mayo, *ibid.*, **61**, 2693 (1939).

The addition products obtained in the experiments summarized in Table II were dehydrobrominated in refluxing anhydrous pyridine and the results are summarized in Table III. The yields in the table correspond to purified products. The refractive index indicates the product to be essentially pure 1-methylcyclohexene (III) and this is confirmed by infrared analysis. Small amounts of an unidentified material were indicated by the infrared analysis. The relative quantities of this material were dependent on the amount of tertiary bromide in the addition product and was not methylenecyclohexane. The latter compound could not be detected in any of the products. In order to demonstrate that III was the initial dehydrobromination product pure 3-methylcyclohexene was submitted to the conditions of the dehydrobromination and recovered unchanged in 91% yield.

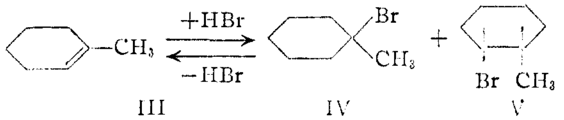
TABLE III

DEHYDROHALOGENATION OF MIXTURES OF 1-BROMO-1-METHYLCYCLOHEXANE AND 1-BROMO-2-METHYLCYCLOHEXANE OBTAINED BY THE ADDITION OF HYDROGEN BROMIDE TO 1-METHYLCYCLOHEXENE

Expt.	*t*-Bromide,[a] %	Yield,[b] %	$n^{25}D$	3-Methylcyclohexene,[c] %
13b	37.6	85.0	1.4482	1.1
14	21.5	78.8	1.4481	1.8
15	22.3	52.3	1.4478	1.1
16	23.4	67.5	1.4478	1.4
18	100.0	92.5	1.4477	0.0

[a] Per cent. 1-bromo-1-methylcyclohexane in material being dehydrobrominated. [b] Yield of purified methylcyclohexene isolated. [c] Infrared analysis.

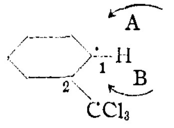
If *trans* dehydrobromination is assumed,[9,16] the data presented in Tables II and III indicate that the 1-bromo-2-methylcyclohexane obtained from the free radical reaction is the *cis* isomer, V. Although all of the addition product is not accounted for in the conversion to methylcyclohexene it appears that at most only a small proportion of the 1-bromo-2-methylcyclohexane could be the *trans* isomer and we have no evidence that any of this isomer is formed. The fact that V is the predominating or exclusive abnormal product indicates that *trans* addition is preferred in this case as well as with I.



III IV V

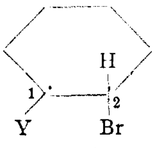
In all of the isolation and purification operations an attempt was made to avoid separation of any possible reaction products. In view of these precautions, together with the results of various control experiments, we feel that the products listed in Tables I, II and III are representative samples of initial reaction products.

Discussion of Results.—Fawcett[17] has pointed out that the results of Kharasch and Friedlander[18] indicate that the *trans* addition product is obtained from the radical chain addition of bromotrichloromethane to cyclohexene and other cyclic systems and suggested that this *trans* addition is due to a preferred direction of approach (A) of the bromotrichloromethane molecule to the intermediate radical VI. This conclusion assumes that A is the preferred direction of approach to C_1 because of the steric effect of the CCl_3 group at C_2, however, models show that if the CCl_3 group occupies the more thermodynamically stable equatorial position[14,19] there is essentially no steric difference between approach from above (A) or below (B) the ring. As *trans* 1,2-disubstituted cyclohexanes are generally thermodynamically more stable than the *cis* isomers,[14,19a] the relative stabilities of the transition states involved in the conversion of VI to the *cis* and *trans* isomers would be expected to be such that the more stable *trans* isomer would be formed preferentially. Inasmuch as the *trans* addition of bromotrichloromethane to cycloalkenes may be a consequence of the relative stabilities of the possible products it cannot be concluded that the addition of radicals to double bonds involves a required or preferred *trans* stereochemical course.



VI

Hydrogen bromide adds *trans* to I and III in spite of the fact that *cis* addition would produce the more thermodynamically stable isomer. This fact indicates that similar to certain ionic additions,[20] the nature of the mechanism of this radical addition to double bonds involves a preferred or required *trans* stereochemical course. *trans* addition cannot be accounted for by the proposed mechanism for chain propagation[3] if the structure of the intermediate radical is assumed to be VII. Indeed a mixture of *cis* and *trans* addition products would be expected from such an intermediate with preponderant formation of the more stable *trans* isomer corresponding to *cis* addition.



VII, Y = CH_3 or Br

In view of the considerable evidence for the proposed propagation reactions[2,3,5] explanations for *trans* addition involving concerted (termolecular) mechanisms seem unattractive.

The *trans* addition suggests that the intermediate radical is not adequately described by VII and the contributing structures usually indicated for a radical of this type.[21] It seems likely that the

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[16] E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 118.

[17] E. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

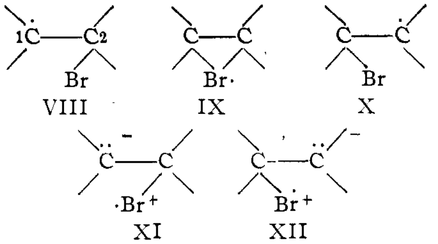
[18] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

[19] (a) D. H. R. Barton, *Experientia*, **6**, 316 (1950). (b) An equatorial position for the C_2 substituent would be more advantageous in VI than in cyclohexane as this places the C_2 hydrogen in a better position for hyperconjugative resonance. See J. D. Roberts, W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3329 (1950).

[20] I. Roberts and G. E. Kimball, *ibid.*, **59**, 947 (1937).

[21] G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., p. 239.

bromine may be centrally located between C_1 and C_2 as this permits stabilization by interaction of the bromine with C_1 as illustrated by the following contributing structures. Structures VIII, X, XI, and XII correspond to three electron bonds.[22] The proposed hybrid radical is analogous to the bromonium ion involved in ionic additions[20] and provides an explanation for the observed *trans* addition as it seems likely that in the second step the hydrogen would become attached to carbon on the side opposite from the bromine bridge.



This formulation is consistent with the orientation of free radical additions of hydrogen bromide as this is governed by the relative importance of VIII and X, which can be assessed from a consideration of the ability of each carbon to tolerate the odd electron.

With this modification the mechanism suggested by Kharasch[3] can accommodate all of the known facts including *trans* addition.

Acknowledgment.—The authors are indebted to Mr. Donald R. Johnson for the infrared analysis.

Experimental

Materials.—Chemically pure anhydrous hydrogen bromide was obtained from the Matheson Co. The benzoyl peroxide was Eastman Kodak Co. "White Label" grade; analysis[23] showed this material to be 91.8% benzoyl peroxide.

The pentane solvent, b.p. 32–35°, was purified by treating Skellysolve A with concentrated sulfuric acid for 24 hours followed by treatment with excess acidified potassium permanganate for 24 hours. The material was distilled from phosphorus pentoxide. The hydrocarbon solvent, b.p. 90°, used in experiment 14 was purified in the same way.

1-Bromocyclohexene (I) was prepared in 10% yield from *trans*-1,2-dibromocyclohexane[13] by the previously described method.[10] The crude material was purified by repeated treatment with hot alcoholic silver nitrate until a precipitate was no longer obtained. After removal of the alcohol and silver nitrate by water extraction the material was fractionated from sodium hydride, b.p. 63.1–63.4° (24 mm.); $n^{25}D$ 1.5117; d^{25}_4 1.386 (lit.[10] b.p. 69° (35 mm.), $n^{20}D$ 1.5134; d^{20}_4 1.3901) *MR* calcd.: 35.01; found: 34.84. This material had the correct analysis for I and yielded adipic acid (60%) when oxidized by neutral permanganate. Under conditions where cyclohexyl bromide gives a heavy precipitate with alcoholic silver nitrate this material showed no sign of reaction indicating that it is 1-bromocyclohexene.

1-Methylcyclohexene (III) was prepared in 60–77% yield according to previously described methods.[24,25] The material was purified by fractionation, b.p. 108.4–108.7°; $n^{25}D$ 1.4478 (lit.[25] b.p. 109–109.5°; $n^{20}D$ 1.4503).

3-Methylcyclohexene, b.p. 100.3–100.7°; $n^{25}D$ 1.4408 (lit.[25] b.p. 100.0–100.8°, $n^{25}D$ 1.4442); was prepared by the method of Arnold, *et al.*[25]

Methylenecyclohexane was prepared from ethyl 1-hydroxycyclohexylacetate[26] according to the method of Wallach.[27] A pure product was obtained in good yields, b.p. 101.9°; $n^{25}D$ 1.4471; d^{25}_4 0.7958 (lit.[28] b.p. 102–103°, $n^{20}D$ 1.4523, d^{20}_4 0.8074).

1-Bromo-1-methylcyclohexane (IV) was obtained by the addition of hydrogen bromide to 1-methylcyclohexene (expt. 18). An identical product was obtained from 1-methylcyclohexanol[25] by the following method: Thirty grams of the alcohol in a flask provided with condenser and drying tube, was saturated with dry hydrogen bromide as the reaction flask was cooled. The reddish-brown reaction mixture was poured into cold water and the organic layer separated. The organic layer was extracted three times with ice cold concentrated sulfuric acid and washed with water. After drying over anhydrous potassium carbonate and sodium sulfate the material was fractionated, b.p. 66.0–66.5° (22 mm.); $n^{25}D$ 1.4468; yield 67.2–79.5%.

Anal. Calcd. for $C_7H_{13}Br$: Br, 45.13. Found: Br, 45.08.

Methods of Addition of Hydrogen Bromide to 1-Methylcyclohexene and 1-Bromocyclohexene. Method A.—A solution of the unsaturated compound in pentane was placed in a 100-ml. glass bomb liner. The quantities of benzoyl peroxide or hydroquinone added were of the order of 5 mole per cent. The solution was chilled and a previously measured volume of liquid anhydrous hydrogen bromide was added and the liner placed in the bomb. The mole ratio of hydrogen bromide to unsaturated compound used was 2:1 for I and 1.3:1 for III. The bomb was sealed and brought to the desired temperature for the time indicated in the tables.

The reaction mixtures were treated with solid sodium bicarbonate with cooling and after the hydrogen bromide had completely reacted the solution was filtered. After removal of the pentane by evaporative distillation through a 30-cm. Vigreux column the product was fractionated with an all glass column with low hold up.

Method B.—The solution of olefin in pentane was placed in a 250-ml. quartz flask equipped with condenser, fritted glass gas bubbler tube and magnetic stirrer. The solution was irradiated with a Hanovia S-100 Scientific Type quartz tube mercury vapor lamp placed 3 in. from the flask. Hydrogen bromide was passed through the solution for the duration of the reaction. The heat generated by the lamp was sufficient to keep the solution refluxing gently. The low concentration of hydrogen bromide in the refluxing solvent necessitated a longer reaction period, but favored free radical addition as compared to ionic addition.[2] In experiments 3 and 17 the flask was partially submerged in ice-water and ice was placed against the flask on the sides away from the lamp. The reaction mixture was worked up as described above.

Method C.—The reaction was carried out in a Pyrex flask provided with condenser, stirrer and gas bubbler tube. Hydrogen bromide was passed through the solution of unsaturated compound in pentane containing added reagents in quantities of 5 mole per cent. Results were the same when the benzoyl peroxide was added in one batch at the start of the reaction as when it was added in three equal portions during the course of the reaction.

Addition of Hydrogen Bromide to 1-Bromocyclohexene.—Addition products with identical refractive indexes and melting points were obtained by methods A and B. In experiment three, hydrogen bromide was added to 5.0 g. (0.031 mole) of I in 150 ml. (1.30 moles) of pentane by method B. After passing hydrogen bromide through the irradiated solution for two hours the pentane was removed by fractionation. The residual oil was fractionated and found to consist of material boiling at 50.5–51.5° (0.13 mm.), $n^{25}D$ 1.5509. The colorless oil, 6.5 g. (86.5% yield) had a melting point of *ca.* 6.5°. Recrystallization from pentane raised the melting point to 9.7–10.5°. Subsequent recrystallizations and distillations did not affect the melting point. When mixed with authentic *trans*-1,2-dibromocyclohexane[13] (m.p. −8.0 to −3.8°) the mixture melted at approximately −40°. We believe this material to be *cis*-1,2-dibromocyclohexane (II).

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[22] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., p. 264.

[23] G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 432.

[24] P. D. Bartlett and R. H. Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

[25] R. T. Arnold, G. G. Smith and R. M. Dodson, *J. Org. Chem.*, **15**, 1256 (1950).

[26] R. L. Shriner in R. Adams, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 17.

[27] O. Wallach, *Ann.*, **365**, 255 (1909).

[28] A. I. Vogel, *J. Chem. Soc.*, 1323 (1938).

Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.78; H, 4.17. Found: C, 30.07; H, 4.27.

The dibromide was dehydrobrominated by refluxing 7.56 g. of material in 10 ml. of 30% alcoholic potassium hydroxide for 12 hours. Addition of water caused 4.09 g. (78%) of product to separate. Distillation of the dried material yielded 3.55 g. (68%) of material that was identified as 1-bromocyclohexene from its physical properties, b.p. 65.7–66.0° (26 mm.), $n^{25}D$ 1.5112.

Five mole per cent. of diphenylamine and ferric chloride were used in experiments 5 and 6 in an attempt to promote ionic addition.[29] In these experiments 90% of the unreacted I was isolated from the deep red solution.

Addition of Hydrogen Bromide to 1-Methylcyclohexene.—A typical experiment is as follows: Experiment 15: Hydrogen bromide was added to 19.25 g. (0.2 mole) of III in 150 g. of pentane according to method B. Dry hydrogen bromide was passed through the solution for 1.25 hours as the solution was being irradiated. After removal of the hydrogen bromide with solid sodium carbonate the solution was filtered and fractionated. After the removal of the solvent and unreacted III the remaining material was completely distilled and collected in three fractions.

Fraction	B.p., °C. (21.5 mm.)	g.	$n^{25}D$	*t*-Bromide, %
1	70.0–72.3	6.57	1.4898	32.6, 32.3
2	72.3–73.3	7.30	1.4905	20.3, 20.9
3	73.3–73.5	5.44	1.4908	12.3, 12.2

The composition of each fraction was determined by analyzing for tertiary bromide in the presence of secondary bromide by the method of Walling, Kharasch and Mayo.[15] Analyses were carried out in duplicate on a 0.1–0.3-g. sample. In this experiment the tertiary bromide amounts to 22.3% of the total product.

In order to check the method of analysis, pure cyclohexyl bromide and 1-bromo-1-methylcyclohexane were analyzed. These analyses showed < 1% tertiary bromide for the former compound and 100% tertiary bromide for the latter.

The fractions were combined and total halogen determined by the method described by Bacon.[30]

Anal. Calcd. for $C_7H_{13}Br$: Br, 45.13. Found: Br, 45.38, 45.11.

The yield of analytically pure material was 19.3 g. (54.5%).

The addition product was dehydrohalogenated as follows: A solution of 11.4 g. of the addition product in 25 ml. of dry pyridine was refluxed for 8 hours and then poured into 100 ml. of water. The solution was neutralized with dilute hydrochloric acid and steam distilled until the distillate contained no unsaturated material. About 15 ml. of distillate was collected. The organic layer was separated and dried and weighed 4.82 g. (78%). This material was distilled yielding 3.23 g. (52.3%) of volatile material, $n^{25}D$ 1.4478. This product was identified as 1-methylcyclohexene containing 1.1% 3-methylcyclohexene by a combination of chemical and infrared analysis. When pure 3-methylcyclohexene was submitted to the conditions of dehydrobromination it was recovered unchanged in 90.8% yield. The experiments summarized in Tables II and III were carried out in a similar manner.

In experiment 18, anhydrous hydrogen bromide was passed through a solution of 15.0 g. of III and 0.15 g. of diphenylamine in 50 ml. of glacial acetic acid. The product was isolated by diluting the solution with water and extracting with pentane. The organic layer was washed with sodium bicarbonate solution and dried over sodium sulfate. Fractionation yielded 23.2 g. (84%) of material, b.p. 66.7–67.7° (23 mm.), $n^{25}D$ 1.4866–1.4868. This material was found to be 100% tertiary halide and appears to be identical with the product obtained from 1-methylcyclohexanol.

Infrared Analysis.—The quantitative determination of 3-methylcyclohexene in III was carried out with a Baird Associates Recording Spectrophotometer with sodium chloride prisms. From the spectra of the pure isomers and of synthetic mixtures containing small amounts of 3-methylcyclohexene, peaks at 13.92 μ and at 14.9 μ were found to be suitable, on the basis of sensitivity and freedom from interference, for the analysis of small amounts of 3-methylcyclohexene in III. As the samples obtained in the dehydrohalogenations contained small and varying amounts of an unidentified impurity absorbing at 14.86 μ the 13.92 μ peak was used for the analysis. A 0.1-mm. cell was used and was calibrated using synthetic mixtures. Beer's law and additivity of absorbencies of solvent and solute were assumed for concentrations of < 6% 3-methylcyclohexene.

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[29] M. S. Kharasch, J. A. Norton and F. R. Mayo, *J. Org. Chem.*, **3**, 48 (1938).

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Condensation of Saturated Halides with Unsaturated Compounds. IX. Halogen Exchange between *t*-Butyl Halides and Aluminum Halides during the Condensation with Ethylene[1]

BY LOUIS SCHMERLING AND JAMES P. WEST

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The condensation of *t*-butyl chloride with ethylene in the presence of aluminum bromide at −40 to −50° results in the formation of 1-bromo- and 1-chloro-3,3-dimethylbutane in 15 and 32% yields, respectively. A similar halogen exchange occurs during the condensation of *t*-butyl bromide with ethylene in the presence of aluminum chloride. Interaction of the alkyl chloride with the catalyst is indicated by these experiments which thus lend support to the carbonium ion theory of metal halide activity. A chain mechanism, involving abstraction of a chloride ion by a carbonium ion, is proposed to explain the data.

The condensation of *t*-butyl chloride with ethylene in the presence of aluminum chloride at −15 to −10° results in a 75% yield of 1-chloro-3,3-dimethylbutane.[2] This reaction presumably occurs by way of polarization of the alkyl halide *via* the formation of a complex with the catalyst. Hence, if the halogen atoms in the catalyst are different from the one in the alkyl halide, it may be expected that at least part of the halogen in the final product will be that of the catalyst rather than of the original *t*-butyl halide

$$(CH_3)_3CCl + AlBr_3 \rightleftharpoons (CH_3)_3C^+(AlBr_3Cl)^- \quad (1)$$

$$(CH_3)_3C^+(AlBr_3Cl)^- + CH_2{=}CH_2 \rightleftharpoons (CH_3)_3CCH_2CH_2^+(AlBr_3Cl)^- \quad (2)$$

$$(CH_3)_3CCH_2CH_2^+(AlBr_3Cl)^- \rightleftharpoons (CH_3)_3CH_2CH_2Br + AlBr_2Cl \quad (3)$$

That such exchange of halogen does occur was shown by an experiment in which ethylene was bubbled into a well-stirred mixture of *t*-butyl

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[1] Preceding paper in this series, THIS JOURNAL, **74**, 2885 (1952).

[2] L. Schmerling, *ibid.*, **67**, 1152 (1945).