Stereochemical Course of the Free-Radical Addition of Hydrogen Bromide to 1-Chloro-4-*t*-butylcyclohexene

P. D. READIO AND P. S. SKELL

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania

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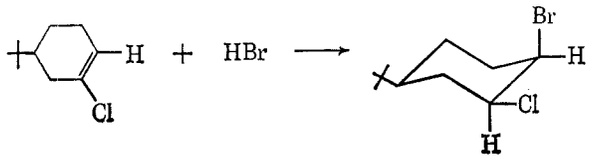
Ionic addition of hydrogen bromide to 1-chloro-4-*t*-butylcyclohexene produces 1-bromo-1-chloro-4-*t*-butylcyclohexane, predominantly with axial bromine. Radical-chain additions are favored by dilution with pentane, at −78° resulting in 95–98% diaxial addition of HBr to produce *trans*-3-bromo-*trans*-4-chloro-*t*-butylcyclohexane (II), the remainder being the *cis*-3-bromo-*trans*-4-chloro-*t*-butylcyclohexane. The radical addition mechanisms are formulated with bromine-bridged radical intermediates, and the unsymmetrical nature of these intermediates is discussed.

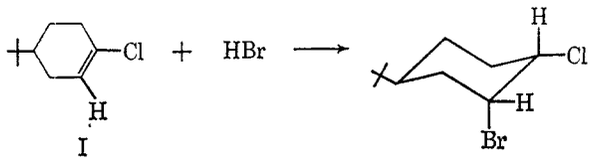
Numerous investigations have been concerned with the stereochemical course of free-radical additions of HBr to olefins. The results of many of these studies have been reviewed by Bohm and Abell.[1] Goering and co-workers[2] studied the stereochemistry of such additions to 1-methyl-, 1-bromo-, and 1-chlorocyclohexene and reported that a nearly exclusive stereospecific *trans* process was occurring. The conclusion that the bromine atom initially approached the double bond from an axial direction was recently confirmed by LeBel and Czaja[3] who found that the addition of HBr to 2-chloro-4-*t*-butylcyclohexene gave only one product, *cis*-3-chloro-*cis*-4-bromo-*t*-butylcyclohexane. We have studied the radical addition of HBr to the related 1-chloro-4-*t*-butycyclohexene.



Results

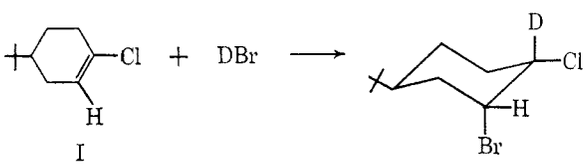
Radical Addition of HBr.—When a pentane solution of HBr (1.7 *M*) and 1-chloro-4-*t*-butylcyclohexene (I) at −78° was irradiated (medium-pressure mercury lamp), the radical reaction proceeded readily to give a good yield of the "abnormal" addition product; distillation followed by vapor phase chromatography (vpc) indicated that only a minor amount (2%) of the normal, 1,1-dihalo, adduct had been formed.

The major product of the radical addition was *trans*-3-bromo-*trans*-4-chloro-*t*-butylcyclohexane (II). It was obtained as a high-boiling liquid. Recrystallization



I II

of adduct II from pentane at −78° yielded a solid, mp 31.5–32.5°. Alkaline dehydrohalogenation of this product to 1-chloro-4-*t*-butylcyclohexene (I) indicated a *cis* relationship of halogens with the bromine axial. Consistent with this assignment was its rate of dehydrohalogenation, $k_2^{24.9} = 6.74 \times 10^{-4}$ l./mole sec. This value compared[4] favorably with that of the related *cis*-1-bromo-2-chlorocyclohexane, $k_2^{25} = 4.52 \times 10^{-4}$ l./mole sec. Further confirmation of the structure of II was provided by its nmr spectrum. As a consequence of the greater coupling constants between axial protons,[5] the cyclohexyl X–C–*H* proton splittings indicate whether the protons are equatorial or axial. Equatorial hydrogens show absorptions which are fairly sharp, essentially unsplit, and relatively narrow at the base, whereas the axial protons are characterized by absorptions with a significant degree of splitting, often a multiplet of seven or eight peaks, and a large base width.[6] The nmr spectrum of II (Figure 1) indicated that the hydrogen on C-3 was equatorial (δ = 277 cps) while that on C-4 was axial (δ = 226 cps). That these absorptions were assigned to the proper hydrogens was verified by inspection of the spectrum of the radical DBr addition product III. The upfield split peak had disappeared, while the low-field absorption (hydrogen equatorial) was still present in the spectrum of III, identifying it as the hydrogen on the bromine-bearing carbon.



I III

The usual liquid state of adduct II suggested the possible contamination of this product by an additional isomer. The presence of a contaminant was verified by vpc; only one other peak was observed. Low-temperature recrystallization of a product mixture concentrated the second adduct in the mother liquor. A weighed portion of this material was heated for 40 min at 100° in an ethanolic NaOH solution. Analysis by vpc indicated that none of the minor component had disappeared, whereas the major component (II) had reacted completely. Treatment of a larger quantity of concentrate in the same manner followed by distillation to remove I yielded the minor adduct free from II. This product was relatively unreactive toward alkaline dehydrohalogenation with $k_2^{82} = 3.1 \times 10^{-5}$ l./mole sec. Since this is not a 1-bromo-1-chloro isomer (*vide infra*), the structure of this adduct

(1) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962).
(2) (a) H. L. Goering, P. I. Abell, and B. F. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952); (b) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).
(3) N. A. LeBel and R. F. Czaja, in press.
(4) H. L. Goering and H. H. Espy, *J. Am. Chem. Soc.*, **78**, 1454 (1956).
(5) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *ibid.*, **80**, 2237 (1958).
(6) N. O. Brace, *ibid.*, **84**, 3020 (1962).

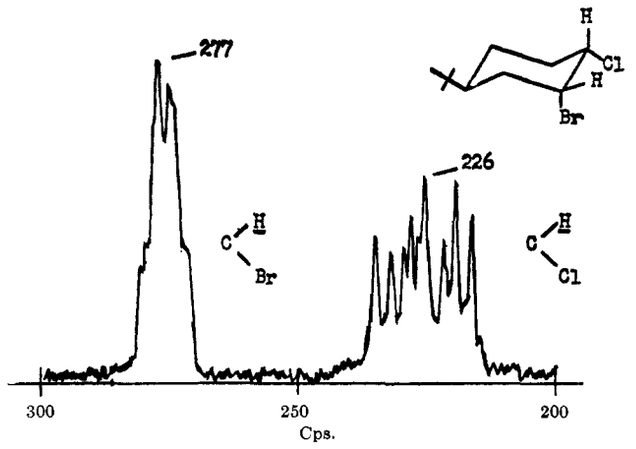


Figure 1.—The nmr spectrum of *trans*-3-bromo-*trans*-4-chloro-*t*-butylcyclohexane (II) (24% in carbon tetrachloride).

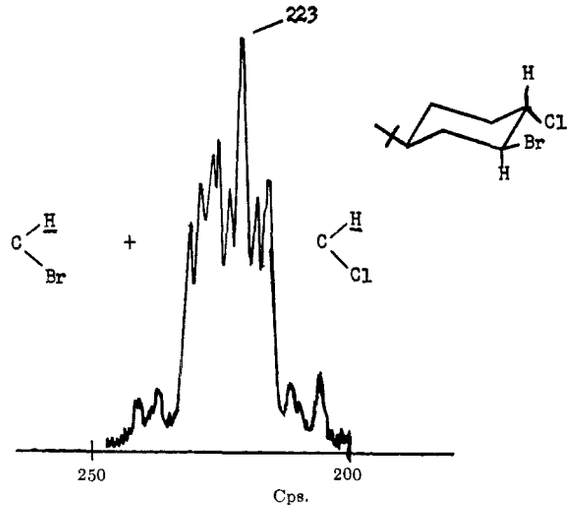
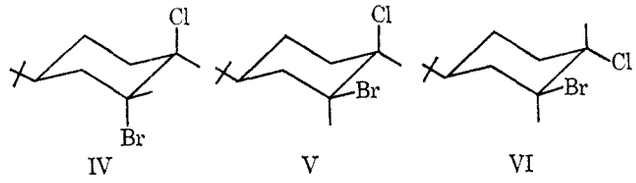


Figure 2.—The nmr spectrum of *cis*-3-bromo-*trans*-4-chloro-*t*-butylcyclohexane (VI).

is one of the following. Estimates of the rate constants for the base dehydrohalogenation of the above dihalides are therefore relevant to the structure assignment of the minor adduct.



IV V VI

Closely related to the structure of IV is the conformation of *trans*-1-bromo-2-chlorocyclohexane with the halogens axial. Since this form is not the favored conformation, the rate constant, $k_2^{79.75} = 3.15 \times 10^{-4}$ l./mole sec,[4] for the alkaline dehydrohalogenation of *trans*-1-bromo-2-chlorocyclohexane represents a minimum value for compound IV. Assuming that loss of the elements H (from C-2) and Br from IV occurs initially and is unaffected by the adjacent chlorine, a better model compound for the estimation of the rate of elimination from IV would be bromocyclohexane: $k_2^{79.75} = 17.0 \times 10^{-4}$ l./mole sec,[4] compensated for a statistical factor of 2 and for the conformational effect (<50% axial bromine). Thus structure IV is not consistent with the slow rate observed for the minor adduct.

The second-order rate constant for base dehydrohalogenation of the *cis* isomer (V) should be at least as great as that for *cis*-1,2-dichlorocyclohexane,[7] $k_2^{79.75} = 28.3 \times 10^{-4}$ l./mole sec,[4] making structure V inconsistent with the slow rate observed for the minor component.

The rate of dehydrohalogenation of VI would be less than that of IV or V since the configuration of the molecule precludes the preferred *trans*-axial relationship between β-H and halogen. This structure appears to be most consistent with the rate observed for the minor adduct in radical addition.

The nmr spectrum is consistent with a *trans*-diequatorial arrangement of halogens in the minor adduct although its interpretation was complicated by the overlapping of the C-3 and C-4 hydrogen peaks (Figure 2). The center of the rather wide absorption was at about 223 cps. Since this represented an upfield shift of the *H*–C–Br absorption (relative to absorption in II) with no apparent change in the position of the *H*–C–Cl peaks, it was concluded that both bromine and chlorine were equatorial.[8] Thus the minor adduct is assigned structure VI, *cis*-3-bromo-*trans*-4-chloro-*t*-butylcyclohexane.

Infrared analysis of a crude product (concentrated by low-temperature recrystallization) before distillation indicated that the minor component, VI, was a product of the addition and not a material resulting from rearrangement. All observed peaks in the infrared spectrum are found in pure II or VI, suggesting that these substances are the only products of radical addition. This conclusion is further supported by the vpc evidence: the presence of only two peaks and the observation that the minor peak is not diminished on treatment with ethanolic NaOH. Since compounds IV and V would have been 90% destroyed during dehydrohalogenation, they could not have contributed significantly to this peak. The relative amounts of the "abnormal" products as determined by vpc were 95% II and 5% VI.

To determine the effect of changing hydrogen bromide concentration on the relative amounts of the adducts II and VI, two crude reaction products were analyzed from additions in which the concentration of HBr was varied by a factor of 32 (Table I). There was essentially no change in the relative amounts of the two adducts.

TABLE I

Mole ratio, HBr/I	HBr, mole/l.	% VI
2.36	0.059	3
3.62	1.9	2

Competition Reaction. Radical Addition of HBr to 1-Chloro-4-*t*-butylcyclohexene (I) and 1-Chlorocyclohexene (IX).—The competitive addition of HBr to olefins I and IX indicated that the *t*-butyl group has

(7) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **78**, 5002 (1956). Effect of the bromine is seen by comparing rate data for 1,2-dibromo- and 1-bromo-2-chloroethane; adjacent bromine facilitates β-hydrogen abstraction to a greater extent than does chlorine by a factor of 1.4.

(8) An axial hydrogen absorption will occur at higher field than that of an equatorial hydrogen on a similarly substituted carbon. L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 115.

TABLE II

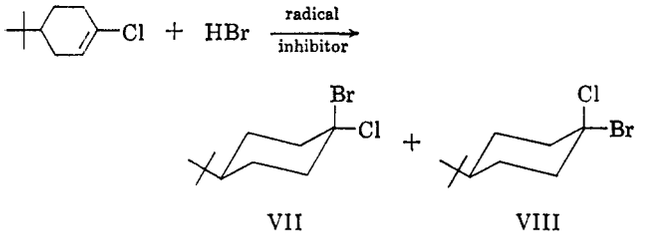
ADDITION OF HYDROGEN BROMIDE TO 1-CHLORO-4-*t*-BUTYLCYCLOHEXENE

Expt	Mole ratio, HBr/olefin	Reaction time, hr	Reaction conditions	% yield of adducts	Mole ratio, (II + VI)/(VII + VIII)
			No Solvent[a]		
1	1.4	4.0	Dark, room temp, $FeCl_3$	66[b]	0
2	1.0	3.0	Dark, room temp, diphenylamine	64	0
3	1.5	8.5	Dark, room temp, radical inhibitor[c]	84	0
4	1.0	3.0	Dark, room temp, ascaridole	69	0
5	1.6	3.25	Ultraviolet, room temp	87	0.008
6	1.6	3.1	Ultraviolet, room temp, ascaridole	86	0.08
7	1.0	3.0	Ultraviolet, room temp	70	0.15
8	0.69	3.4	Ultraviolet, room temp	85	3.1
9	0.10	3.0	Ultraviolet, room temp	64	6.6
10	1.0	4.5	Ultraviolet, −78°	43	0.91
11	...[d]	4.0	Ultraviolet, −78°	16	>100
			Pentane as Solvent		
12	...[e]	4.7	Ultraviolet, −78°, ascaridole	82	13.4
13	1.9[f]	1.0	Ultraviolet, −78°	77	62

[a] Pressure-tube reactions except for expt 11. [b] Some of the reaction mixture spilled. [c] 4,4′-Bis(2,5-di-*t*-butylphenol). [d] Low HBr pressure was maintained above olefin. [e] HBr was bubbled into pentane solution of olefin. [f] HBr concentration, 1.7 *M*.

a negligible effect on the addition. The ratio of rate constants, k_{IX}/k_I, was equal to 2.0.

Ionic Addition of HBr.—The ionic addition of HBr to I occurred readily (several hours) in a pressure tube at room temperature. At low concentrations of HBr the radical process competed with the normal addition, see Table II. When the reaction was effected in the dark in the presence of ferric chloride or a radical inhibitor, *cis*-4-bromo-*trans*-4-chloro-*t*-butylcyclohexane (VII) and *trans*-4-bromo-*cis*-4-chloro-*t*-butylcyclohexane (VIII) were the only products. Infrared analysis indicated that adducts II and VI were not produced. The major substance resulting from ionic addition was adduct VII, estimated 85–90% (infrared). The 1,1-dihalo structure of this substance was assigned as a result of its hydrolysis to 4-*t*-butylcyclohexanone. Further support was obtained from the nmr spectrum, which showed no downfield peaks characteristic of *H*–C–Br and *H*–C–Cl absorptions.



VII VIII

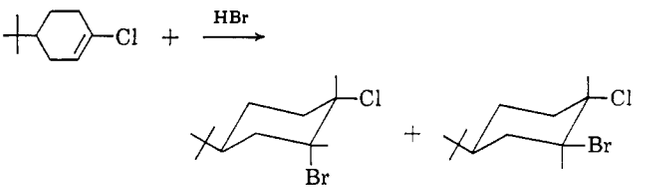
Alkaline dehydrohalogenation of the major component, VII, yielded 1-chloro-4-*t*-butylcyclohexene (I) through loss of the elements H and Br suggesting an axial position for bromine in VII. The second-order rate constant for the process, $k_2^{75.9} = 24.2 \times 10^{-4}$ l./mole sec, agrees with the values reported for 1-bromo-1-chlorocyclohexane, $k_2^{75.9} = 22.2 \times 10^{-4}$ l./mole sec, and 1,1-dibromocyclohexane, $k_2^{75.9} = 19.5 \times 10^{-4}$ l./mole sec, but differs considerably from that reported for 1,1-dichlorocyclohexane, $k_2^{75.9} = 0.485 \times 10^{-4}$ l./mole sec.[4]

The crude reaction product had weak infrared absorption bands not assignable to VII; these were attributed to VIII. In the absence of $FeCl_3$ catalyst, VIII was a minor product; in the presence of $FeCl_3$ VIII comprised 30% of the addition product. This substance was concentrated by alkaline dehydrohalogenation of a product mixture, which preferentially destroyed the major component (VII). Distillation to remove I left a liquid residue insufficient for further purification. The infrared absorptions of this material matched the minor absorptions in the crude product and indicated VII had been destroyed completely. The spectrum of VIII is similar to that of VII except for shifts in the absorption maxima of the 11–14-μ region. The nmr spectrum of VIII was also consistent with a 4-bromo-4-chloro structure; the slower rate of dehydrohalogenation suggested in axial position for chlorine.

Discussion

The free-radical addition of hydrogen bromide to 1-chloro-4-*t*-butylcyclohexene proceeds in the following manner.

Although one might write mechanisms to account for these results employing only classical radicals, the evidence for bridged bromoalkyl radicals dictates that such species be incorporated into the mechanistic scheme for this addition as well as for other instances



II 95% VI 5%

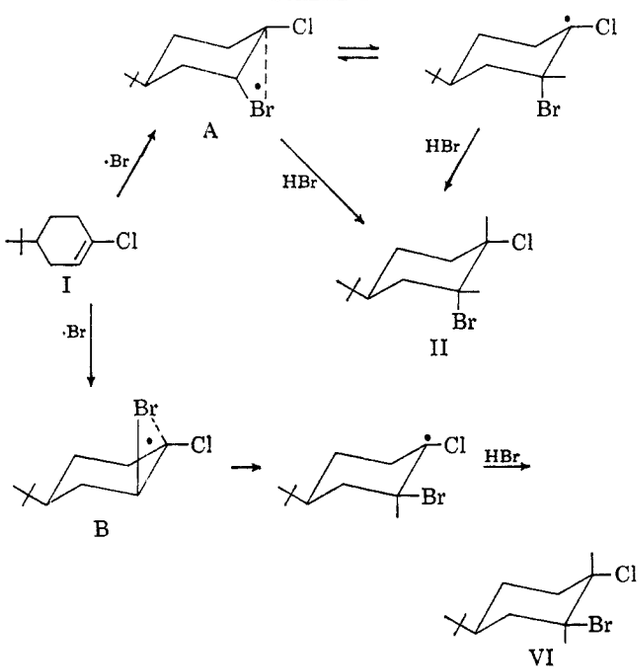
where steric control operates in HBr additions. Experiments involving photobromination of *cis*-4-bromo-*t*-butylcyclohexane[9a] and (+)-1-bromo-2-methylbutane[9b] clearly indicate that a bromine atom adjacent to a radical site can effectively control the stereochemistry at the radical-bearing carbon.

(9) (a) P. S. Skell and P. D. Readio, *J. Am. Chem. Soc.*, **86**, 3334 (1964); P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).

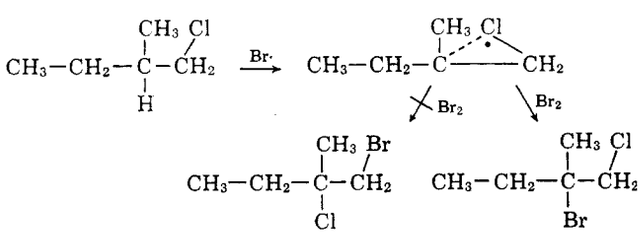
The formation of the minor adduct VI results from initial bromine bridging on the side of the double bond *cis* to the *t*-butyl group. The transfer of a hydrogen atom to this bridged form (B) would have produced *cis*-3-bromo-*cis*-4-chloro-*t*-butylcyclohexane (V) rather than VI. This requires that the bridged form open to a classical radical, accessibility of HBr approach and product stability both influencing the hydrogen abstraction to occur preferentially to the axial position. The formation of the major adduct II requires initial bridging of bromine on the side of the double bond *trans* to the *t*-butyl group; reaction to abstract hydrogen then occurs rapidly with the bridged intermediate. However, the alternative process of bridge opening and reaction of the classical radical to give axial hydrogen preferentially is not ruled out by the results.

The processes representing the additions are shown in Scheme I. The absence of any significant difference in the ratio of products on change of hydrogen bromide concentration suggests that the bridged radicals do not return to I in the presence of HBr.

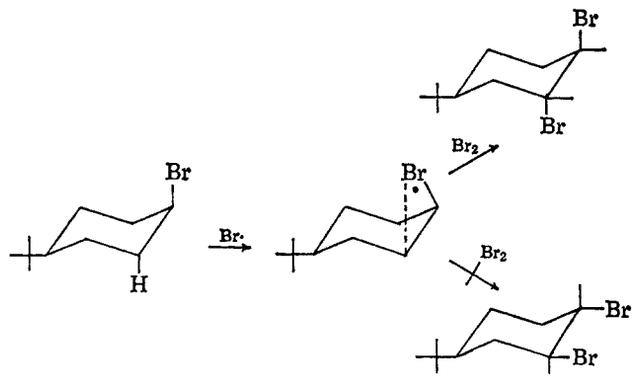
SCHEME I



Halogen bridging in radicals is often unsymmetrical. Electronic and steric effects have been recognized as the origins of this asymmetry. The clearest instances indicating these effects are the photobrominations of (+)-2-methyl-1-chlorobutane[9b] and *cis*-4-bromo-*t*-butylcyclohexane.[9a]



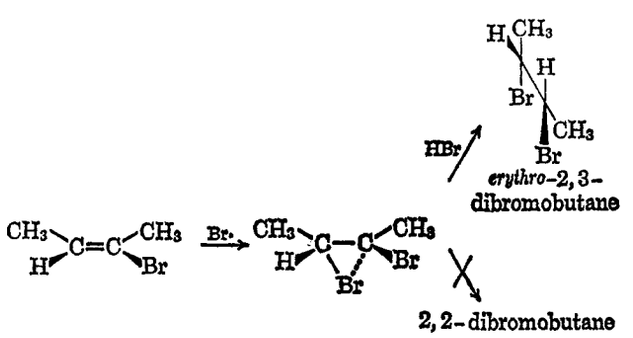
The bromination of active amyl chloride[9b] is stereospecific to the (−)-1-chloro-2-bromo compound, indicating the preference for Br_2 attack at the tertiary position. It is reasonable that in the bridged intermediate the bond to the primary atom is stronger than the bond to the tertiary atom, leaving more radical character (unpaired electron) on C-2. This is the electronic effect, and stated in general terms, *the bridge is unsymmetrical in the direction which favors the more stable of the two unbridged radicals.*



The attack of Br_2 on the bridged radical in photobromination of *cis*-4-bromo-*t*-butylcyclohexane[9a] occurs at C-3 and not at C-4. Attack at C-4 requires a boat-form transition state, while attack at C-3 follows a lower energy path which maintains the more stable chair form in the transition state leading to the diaxial product. Here is an instance of *unsymmetrical reactivity which has its origins in the different steric strains of the two transition states.*

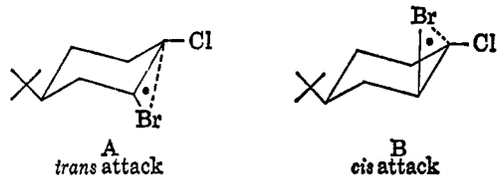
Analogous effects are well established in the acid-catalyzed hydrolyses of epoxides such as propylene oxide *via* the more stable carbonium ions and the reactions of cyclohexane-type oxides which occur to give diaxial opening of the epoxide ring.

The additions of hydrogen bromide to *cis*- and *trans*-2-bromo-2-butene[10] provide another instance of unsymmetrical bridging in an acyclic system. Stereospecific addition is best explained with an unsymmetrical bridged intermediate, resonance stabilization of the α-halo radical resulting in greater radical character at the bromine-bearing carbon.

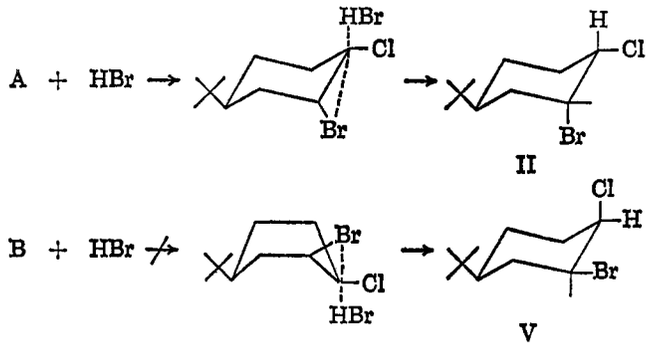


Applying the above ideas to the mechanism proposed for additions of HBr to 1-chloro-4-*t*-butylcyclohexene, it is possible to account for the predominant formation of II, the adduct resulting from initial bridging *trans* to the *t*-butyl group. Both factors which make bridging unsymmetrical are operative and apply in concert to direct the formation of II. The α-chloro radical is resonance stabilized and therefore more stable than the secondary cycloalkyl radical. This effect predicts an asymmetry in the intermediates as shown. Diaxial opening by attack of HBr at C-4

(10) H. L. Goering and D. W. Larsen, *J. Am. Chem. Soc.*, **81**, 5937 (1959).



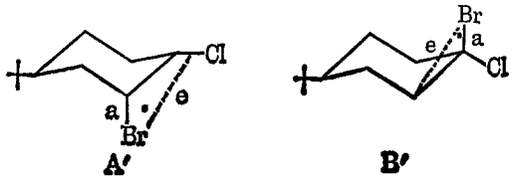
is possible for A, but not for B. If B did react, it would produce V, a product not observed. For B the lower energy path is ring opening to the classical



radical; the preference of addition from the axial direction has been observed in unbridged cyclohexyl radicals, thus accounting for the formation of VI (and probably V, but in amounts too small to detect).[11]

The competitive addition of hydrogen bromide to 1-chlorocyclohexene (IX) and 1-chloro-4-*t*-butylcyclohexene (I) indicates that the *t*-butyl group has no effect on the addition. The ratio of rate constants, k_{IX}/k_I, is 2.0. The relative rates of addition (a) to the double bond in 1-chlorocyclohexene, (b) to the double bond in I from the direction *trans* to the *t*-butyl group, and (c) to the double bond on the side *cis* to the *t*-butyl group are therefore 2.0:0.95:0.05, respectively. It is possible that in the absence of a large group, such as *t*-butyl, the double bond in a cyclohexene is equally reactive to attack from either direction. With 1-chloro-4-*t*-butylcyclohexene, a stereoelectronic effect may account for the low reactivity for bromine attack *cis* to the *t*-butyl group.

The factor of 19 to 1 in favor of Br· adding *trans* to the *t*-butyl group may indicate another source of bridge asymmetry, illustrated below, showing the axial bridge bonds stronger than the equatorial bridge bonds. If this hypothesis is correct, the preference for



formation of A′ over B′ can be explained, since structure A′ makes more effective use of the stabilizing effect of the chlorine by maximizing the free-electron density on C-4. This conjecture is the subject of further investigation.

(11) One referee suggests that classical radicals are the primary products and only the bromine in axial position subsequently bridges. There is no basis in this work for distinguishing these hypotheses. With acyclic olefins the primary step leads to a bridged intermediate in some instances, in others to open-chain intermediates. Analogy brings the authors to the proposed order of events rather than the reverse.

Experimental Section

Nmr Spectra.—Nmr spectra were obtained with a Varian A-60 nmr high-resolution spectrometer. In all cases tetramethylsilane (TMS) was used as an internal standard and shifts in cycles per second are referred to it.

Vapor Phase Chromatography.—For the determination of the relative amounts of adducts II and VI, a Barber-Coleman Model 20 (ionization detection system) chromatograph equipped with a 100 ft × 0.01 in. (i.d.) stainless steel Golay column (dioctyl phthalate) was utilized. Other vpc analyses were obtained with an F & M Model 202 programmed-temperature gas chromatograph equipped with a 5 ft × 0.25 in. (o.d.) column with a packing of 0.75% fluorosilicone on 80–100 mesh Gas-Chrom S.

1-Chloro-4-*t*-butylcyclohexene (I).—A procedure similar to that of Mousseron and Jacquier[12] was used. A solution of 4-*t*-butylcyclohexanone (100 g, 0.649 mole) in 200 ml of dry ether was added over 1.25 hr to a stirred suspension of phosphorus pentachloride (162 g, 0.778 mole) in 300 ml of ether. The mixture was warmed to a slow rate of reflux and stirred for 2 hr more. The mixture was poured over cracked ice, the temperature staying about −10°. The organic layer was separated and the aqueous layer extracted once with 300 ml of ether. The combined ether solutions were washed with 10% $NaHCO_3$ and water, and then dried over Na_2SO_4. Removal of the ether by distillation and vacuum distillation of the residue through a spinning-band column (24 in.) yielded 90.6 g (81% yield) of 1-chloro-4-*t*-butylcyclohexene (I), bp 82.5–83.0° (7 mm), $n^{25}D$ 1.4772.

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.54; H, 9.92. Found: C, 69.68; H, 10.00.

Free-Radical Addition of HBr to 1-Chloro-4-*t*-butylcyclohexene. A.—A stirred solution of 1-chloro-4-*t*-butylcyclohexene (I) (22.2 g, 0.129 mole), HBr (19.8 g, 0.245 mole), and 115 ml of pentane in a Vycor flask attached to a Dry Ice condenser was maintained at −78° and irradiated for 1 hr, using a medium-pressure mercury lamp (400 w, Westinghouse). The reaction mixture was allowed to warm slightly, causing evolution of excess HBr, and was then washed with 10% $NaHCO_3$ and water. The pentane solution was dried over Na_2SO_4 and the pentane was removed by distillation. The material remaining was distilled through a spinning-band column (24 in.) (Table III). A 77% yield of adducts (theoretical yield, 32.7 g) was obtained. The relative quantities of adducts were determined in the following manner.

TABLE III

Fraction	Wt, g	Head temp, °C	Pressure, mm	$n^{25}D$
1	0.91	47–71	0.25	1.4853
2	3.15	64–69	0.10	1.5021
3	4.48	67.5–68	0.10	1.5056
4, 5	16.91	71.0–71.5	0.13	1.5060
6	1.01	Residue		

The infrared spectrum of fraction 1 contained absorptions attributable to olefin I, *trans*-3-bromo-*trans*-4-chloro-*t*-butyl cyclohexane (II), and *cis*-4-bromo-*trans*-4-chloro-*t*-butylcyclohexane (VII). The remaining fractions had spectra characteristic of II.

Analysis by vpc was accomplished using two columns. The fluorosilicone column (programmed from 125° at 2.5°/min) gave a chromatogram with peaks due to the olefin (I), the ionic product (VII), and the 3-bromo-4-chloro product (II and VI). The peaks due to I and VII were identified by their collection and analysis by infrared spectroscopy. Analysis of each distillation fraction indicated that approximately 1–2% of the addition product was the ionic adduct VII. A dioctyl phthalate Golay column at 142° was then used for analysis of each fraction to determine the relative amounts of II and VI. Area measurements indicated 4.6% of adduct VI and 95.4% of adduct II.

Some of the fractions solidified to give crystalline II. On recrystallization from pentane at −78°, white crystalline II was obtained with mp 31.5–32.5°. (*Anal.* Calcd for $C_{10}H_{18}BrCl$: C, 47.35; H, 7.15. Found: C, 47.21; H. 7.17.) Treatment of a sample of adduct II with 80% ethanolic NaOH (0.1 *M*) at 75° for 3 hr gave a material which had an infrared spectrum virtually identical with that of 1-chloro-4-*t*-butylcyclo-

(12) M. Mousseron and R. Jacquier, *Bull. Soc. Chim. France*, 648 (1950).

hexene. The spectrum contained no additional absorptions of significant intensity.

A radical product mixture of II and VI from a previous addition was recrystallized from pentane at −78°. Isomer VI was concentrated in the mother liquor. The pentane was removed under reduced pressure to give a liquid whose vpc (Golay column at 150°) indicated peaks due to VI and II with retention times of 47.2 and 50.2 min, respectively. A portion of the liquid (0.559 g) and 0.05 g of decalin were dissolved in 45 ml of 80% ethanol (approximately 0.1 *M* in NaOH) and the solution, in a pressure bottle, was maintained at steam-bath temperature for 40 min. The solution was then poured into dilute acid and the resulting mixture was extracted with ether. After the extracts had been washed and dried, the ether was removed and a vpc (Golay column at 140°) was obtained. Comparison of this vpc with one taken of the product mixture before dehydrohalogenation indicated that isomer II had reacted completely, whereas adduct VI was essentially unchanged. The vpc data are given in Table IV.

TABLE IV

	Peak height		Ratio, Height of decalin peak/ height of component peak	
Component	Before	After	Before	After
Decalin	60.0	95.3	1	1
VI	26.7	45.5	2.25	2.09
II	40.6	0	1.48	...

Low-temperature recrystallization (−78°) of fractions 2–5 (Table III) from pentane concentrated adduct VI in the mother liquor. Removal of the pentane and treatment of the concentrate (1.87 g) with alcoholic base employing the same conditions as above yielded olefin I and VI. Adduct VI was then obtained by distillation, bp 82° (0.1 mm), $n^{25}D$ 1.5039. (*Anal.* Calcd for $C_{10}H_{18}BrCl$: C, 47.35; H, 7.15; mol wt, 253.6. Found: C, 48.64; H, 7.19; mol wt, 254.) A 24% solution of adduct VI in CCl_4 gave an nmr spectrum which showed one split peak downfield of the cyclohexyl ring protons (Figure 2). Determination of the relative area of this peak to that of the *t*-butyl peak (area of *t*-butyl peak/area of 205–242-cps absorption = 4.3/1 as measured by an A-60 integrator) indicates that the downfield absorption represents two protons.

B.—A solution of 75 ml of pentane, 1-chloro-4-*t*-butylcyclohexene (15 g, 0.087 mole), and HBr (9 g, 0.1 mole) in a quartz flask was maintained at −78°. A Dry Ice condenser was attached to the flask and the system was kept under positive helium pressure. The stirred solution was irradiated for 30 min with a medium-pressure mercury lamp. Solid II formed during the reaction. After it had melted, solid K_2CO_3 was added. The pentane solution was filtered and then cooled to −78°. A crystal of II was added, causing a white precipitate to form. The mother liquor was removed and concentrated to yield a product with an infrared spectrum which was a composite of the spectra of olefin I, adduct II, and adduct VI. The spectrum contained no extraneous absorptions in the 10–16-μ region.

C.—A quartz flask containing 200 ml of pentane and equipped with a Dry Ice condenser and gas inlet tube was immersed in a Dry Ice–acetone bath. Gaseous HBr (300 cc, 0.0118 mole) was collected in a gas buret (mercury) and then condensed in the cold pentane solution. 1-Chloro-4-*t*-butylcyclohexene (0.86 g, 0.005 mole) was added and the stirred solution at −60 to −70° was irradiated with a medium-pressure mercury lamp for 30 min. The pentane and excess HBr were removed under reduced pressure. Analysis of the residue by vpc (fluorosilicone column) indicated virtually complete reaction. Analysis employing the capillary unit (dioctyl phthalate column at 130°) indicated 3% of adduct VI and 97% of adduct II.

D.—Hydrogen bromide (17 g, 0.21 mole) was condensed in 94 ml of pentane in a quartz flask at −78°. 1-Chloro-4-*t*-butylcyclohexene (10 g, 0.058 mole) was added and the stirred solution was irradiated for 30 min with a medium-pressure mercury lamp. Removal of the excess HBr and the pentane gave a crude product which was analyzed with the same Golay column and under the same conditions as above. The analysis indicated that the addition had been virtually complete and showed that the product contained roughly 2% of adduct VI and 98% of adduct II.

Preparation of *trans*-3-Bromo-*trans*-4-chloro-*cis*-4-deuterio-*t*-butylcyclohexane (III).—Deuterium bromide, prepared by addition of D_2O to boron tribromide, was passed into a solution of 100 ml of pentane and 1-chloro-4-*t*-butylcyclohexene (8.1 g, 0.047 mole) in a Vycor flask at −78°. The flask was attached to a Dry Ice condenser and the stirred solution was irradiated with a medium-pressure mercury lamp for 30 min. Distillation of the product through a 15-cm Vigreux column yielded 6.9 g of adduct III, bp 80–81° (1 mm), $n^{25}D$ 1.5042–1.5049. Recrystallization from cold pentane gave a solid, mp 31.0–32.2° (mmp of III and II 31.2–32.4°). This adduct was converted to 1-chloro-4-*t*-butylcyclohexene (I) on treatment with ethanolic NaOH.

Ionic Addition of HBr to 1-Chloro-4-*t*-butylcyclohexene. A. With Radical Inhibitor.—A pressure tube [approximately 40-cc volume prepared from 25 mm (o.d.), 3 mm (thickness) glass tubing] containing 1-chloro-4-*t*-butylcyclohexene (25.9 g, 0.15 mole) and 4,4′-bis(2,6-di-*t*-butylphenol) (0.27 g) was attached to a vacuum line. After the contents had been degassed, HBr (0.229 mole) was condensed in the tube at −195° and the tube was sealed. It was warmed to room temperature and kept in the dark for 8.5 hr. The tube was then cooled, opened, and again attached to the vacuum line in order to remove the excess HBr (0.082 mole). Distillation of the product mixture through a spinning-band column (24 in.) yielded a forerun (1.35 g, $n^{25.2}D$ 1.4857) and four fractions (31 g, 84% yield), bp 80.0–81.0° (2 mm), $n^{25.2}D$ 1.4928–1.4963. Infrared spectra of the fractions and the residue indicated that *cis*-4-bromo-*trans*-4-chloro-*t*-butylcyclohexane (VII) was the predominant product (85–90%) with *trans*-4-bromo-*cis*-4-chloro-*t*-butylcyclohexane (VIII) suggested as a minor adduct. There was no evidence in these spectra for the presence of adducts II and VI.

One fraction (distillation of another ionic addition product), which was predominately adduct VII, had bp 66–67° (0.5 mm), $n^{27}D$ 1.4961.

Anal. Calcd for $C_{10}H_{18}BrCl$: C, 47.35; H, 7.15. Found: C, 47.62; H, 7.08.

Dehydrohalogenation of adduct VII was accomplished by treating a sample for several days with ethanolic NaOH at 75°. Acidification of the reaction mixture followed by ether extraction yielded a yellow solution, which was washed with water, dried, and concentrated. The infrared spectrum of the product was virtually identical with that of 1-chloro-4-*t*-butylcyclohexene.

Adduct VII was hydrolyzed to 4-*t*-butylcyclohexanone by refluxing a mixture of adduct VII (13 g, 0.052 mole), $BaCO_3$ (11 g), and 65 ml of water for 17 hr. The $BaCO_3$ was decomposed with HCl and the mixture was extracted with ether. Removal of the ether yielded approximately 5 g of a liquid which formed a 2,4-dinitrophenylhydrazone (2,4-DNPH), mp 149–150°. The 2,4-DNPH of 4-*t*-butylcyclohexanone was prepared, mp 149–150°.

The nmr spectrum of a neat sample of adduct VII showed no absorptions downfield of 180 cps. The peak due to the *t*-butyl protons absorbed at 55 cps, while the absorptions of the cyclohexyl ring protons were continuous through the region 65–180 cps.

B. With Ferric Chloride.—The procedure was essentially the same as in A. 1-Chloro-4-*t*-butylcyclohexene (19.4 g, 0.113 mole), HBr (0.163 mole), and ferric chloride (0.15 g) were sealed in a pressure tube. After 4 hr at room temperature, the tube was cooled and opened; a quantity of 0.057 mole of HBr was recovered. Distillation of the product (some spilled in transfer) through an 11-cm Vigreux column yielded five fractions (18.7 g, 65% yield), bp 64–69° (1 mm), $n^{25.8}D$ 1.4908–1.4977. Infrared spectra of all fractions and the residue indicated no evidence for adducts II and VI. Adduct VII was still the predominant product, although the quantity of adduct VIII was greater than observed above (estimated to be about 30%). Partial fractionation of VII and VIII had occurred as indicated by increased absorption in the 13.85–13.95- and 12.03–12.08-μ regions of the infrared spectra of the latter fractions. The infrared spectrum of fraction 2 had a peak at 12.01 μ (VII) with a shoulder in the 12.03–12.08-μ range, whereas that of fraction 5 had a peak at 12.09 μ (VIII) with the shoulder in the 12.01–12.06-μ region.

Treatment of a mixture of VII and VIII with alcoholic NaOH (88% ethanol, 0.5 *M* NaOH, 0.47 *M* organic halide at 50° for 16 hr) followed by distillation to remove 1-chloro-4-*t*-butylcyclohexene yielded a small quantity of residue (VIII) with $n^{25}D$ 1.4983. The infrared absorptions of the residue corresponded

to those minor absorptions in the spectra of the product mixtures. The infrared spectra of VII and VIII were nearly superimposable except for slight differences in wavelength for absorptions between 11 and 14 μ.

The nmr spectrum of a CCl_4 solution of VIII showed no peaks downfield of 178 cps. The cyclohexyl ring protons absorbed continuously throughout the region 59–178 cps, while the *t*-butyl protons had a shift of 53 cps.

Competitive Addition of HBr to 1-Chloro-4-*t*-butylcyclohexene (I) and 1-Chlorocyclohexene (IX).[13]—1-Chloro-4-*t*-butylcyclohexene (17.25 g, 0.100 mole), 1-chlorocyclohexene (11.65 g, 0.100 mole), and 88 ml of pentane were placed in a quartz flask. A Dry Ice condenser was attached and flask was immersed in a −78° bath. Hydrogen bromide (8.4 g, 0.10 mole) was condensed in the cold pentane solution and this stirred solution was irradiated for 1 hr using a medium-pressure mercury lamp. Analysis of the product mixture by vpc (fluorosilicone column at 125° with programming at approximately 2.5°/min) indicated that the area of the *cis*-1-bromo-2-chlorocyclohexane (X)[15] peak was 58.3% of the combined area of the two adduct peaks (II and X). Using the same vpc conditions as above, the relative response of the adducts was determined by analysis of a mixture of known composition of II and X. Applying this correction to the area measurement of the product mixture, it was found that the molar ratio, X/II, was 1.63/1.0.

Assuming complete reaction of HBr, the ratio of rate constants for reaction of each olefin with HBr can be calculated from the expression

$$\frac{k_{IX}}{k_I} = \frac{\log \frac{[IX]_i}{[IX]_f}}{\log \frac{[I]_i}{[I]_f}} = \frac{\log \frac{0.1}{0.038}}{\log \frac{0.1}{0.062}} = 2.0$$

(13) 1-Chlorocyclohexene was prepared by a procedure which was essentially that of Mousseron and Jacquier.[12] A 45% yield of IX was obtained: bp 77.0–78.3° (98 mm), $n^{25}D$ 1.4783 [lit. bp 50° (20 mm),[11] 63–65° (61 mm);[13] $n^{25}D$ 1.4772,[11] 1.4784[13]].

(14) H. L. Goering, D. I. Relyea, and D. W. Larsen, *J. Am. Chem. Soc.*, **78**, 348 (1956).

(15) *cis*-1-Bromo-2-chlorocyclohexane, bp 64–66° (1 mm), $n^{25}D$ 1.5230, was prepared by the ultraviolet-initiated addition of HBr to 1-chlorocyclohexene in pentane [lit.[2b] bp 87.5–88° (7 mm), $n^{25}D$ 1.5238].

Determination of Rate Constants for Alkaline Dehydrohalogenation. A. Dehydrobromination of *trans*-3-Bromo-*trans*-4-chloro-*t*-butylcyclohexane (II).—A solution of adduct II (0.0647 *M*) and 80% ethanol (0.1012 *M* in NaOH) was prepared in a volumetric flask which was placed in a bath at 24.92 ± 0.04°. Aliquots were removed periodically and pipetted into dilute nitric acid. After extraction of the resulting mixture with CCl_4, analysis of the aqueous layer for bromide was accomplished using the Volhard procedure. Eleven determinations involving 8–46% reaction gave $k_2 = (6.74 \pm 0.16) \times 10^{-4}$ l./mole sec.

B. Dehydrobromination of *cis*-4-Bromo-*trans*-4-chloro-*t*-butylcyclohexane (VII).—A solution of adduct VII (0.0496 *M*) and 80% ethanol (0.0973 *M* in NaOH) was apportioned among ampoules which were sealed and placed in an oil bath at 75.90 ± 0.02°. After the desired intervals of time, the ampoules were removed and plunged into ice–water. Aliquots were added to dilute nitric acid and analysis for bromide was accomplished as above. Eight determinations involving 14–63% reaction gave $k_2 = (24.2 \pm 1.6) \times 10^{-4}$ l./mole sec. The values of the rate constants showed a downward trend with increasing reaction more than likely indicating contamination by the less reactive adduct (VIII).

C. Dehydrohalogenation of *cis*-3-Bromo-*trans*-4-chloro-*t*-butylcyclohexane (VI).—A solution of adduct VI (0.0388 *M*) and 80% ethanol (0.101 *M* in NaOH) was prepared in a 25-ml volumetric flask. This solution was transferred to an alkali-resistant flask which was placed on a steam bath. The solution was refluxed (temperature approximately 82°) for the desired length of time and then cooled to room temperature for removal of an aliquot. Analysis for halide after 230, 545, and 2090 min indicated 7 to 23% reaction, assuming loss of 1 equiv of HX. The second-order rate constant was calculated, $k_2 = 3 \times 10^{-5}$ l./mole sec (average of three values, 4.9, 2.5, and 1.9×10^{-5}).

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Stereochemistry of the Free-Radical Addition of Methyl Mercaptan to 1-Chloro-4-*t*-butylcyclohexene

P. D. READIO AND P. S. SKELL

Department of Chemistry, the Pennsylvania State University, University Park, Pennsylvania

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The major product from radical-chain addition of methyl mercaptan to 1-chloro-4-*t*-butylcyclohexene is *trans*-3-methylmercapto-*trans*-4-chloro-*t*-butylcyclohexane (II), the result of diaxial addition; the other three isomers have been identified as minor products (12% total). The role of 1,2-sulfur bridging is discussed.

Free-radical thiol additions are generally less stereospecific than the additions of hydrogen bromide involving analogous systems. Additions to cyclic systems (except bridged bicyclic) show a preference for *trans* addition, although complete stereospecificity has not been reported. The reactions with acyclic molecules are essentially nonstereospecific. For the most part, the stereochemical results are rationalized by a mechanism involving classical radicals, with the lack of specificity attributed to the slow chain-transfer step. Isomerizations of alkyl radicals and even conformational changes in cyclic intermediate radicals are presumed to occur before the hydrogen-abstraction process is completed. The absence of complete specificity in thiol reactions has created little enthusiasm for a mechanism involving bridged sulfur radical intermediates. Those investigations of thiol additions completed before 1940 were summarized by Mayo and Walling,[1] while the more recent results have been described by Walling.[2] Work involving the stereochemical aspects have also been well reviewed by Bohm and Abell.[3]

More recently, Le Bel and Czaja have investigated the radical additions of thiophenol, hydrogen sulfide, and thiolacetic acid to 2-chloro-4-*t*-butyl-cyclohexene.[4] The product of *trans*-diaxial addition was the predominant adduct observed in each case, although products

(1) F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940).

(2) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(3) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962).

(4) N. A. Le Bel and R. F. Czaja, in press.