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Conformational Analysis. V. The Reaction of *cis*- and *trans*-4-*t*-Butylcyclohexanol and *trans*-4-Methylcyclohexanol with Phosphorus Pentabromide. Syntheses of Alkylcyclohexyl Bromides[1]

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Reaction of *cis*-4-*t*-butylcyclohexanol with phosphorus pentabromide gives *trans*-4-*t*-butylcyclohexyl bromide, a mixture of 1-, 3-, and 4-*t*-butylcyclohexenes and a dibromide which appears to be *trans*-3-*cis*-4-dibromo-*t*-butylcyclohexane. An easier route to *trans*-4-*t*-butylcyclohexyl bromide involves catalytic hydrogenation of 4-*t*-butylbenzoic acid followed by a Hunsdiecker reaction to give a mixture of *cis*- and *trans*-4-*t*-butylcyclohexyl bromides rich in the latter; the *cis*-contaminant may be removed by preferential destruction by base. *trans*-4-*t*-Butylcyclohexanol and phosphorus pentabromide yield *cis*-4-*t*-butylcyclohexyl bromide (which may be purified by crystallization) and a small amount of a position isomer, as well as a dibromide fraction apparently consisting of a major amount of *cis*-3-*trans*-4-dibromo-*t*-butylcyclohexane and a minor amount of the *trans*-3-*cis*-4 isomer. A mixture of the same two dibromides but in reversed proportion is obtained by the addition of bromine to 4-*t*-butylcyclohexene.

Reaction of commercial (*trans*-rich)-4-*t*-butylcyclohexanol with hydrogen bromide leads to a complex mixture of positional as well as configurational isomers. Treatment of *trans*-4-methylcyclohexanol, obtained by fractional distillation of the commercial *cis*-*trans* mixture, with phosphorus pentabromide leads to *cis*-4-methylcyclohexyl bromide among other products. The stereochemical and mechanistic implications of these results are discussed.

In connection with another problem[2] we have studied the preparation of *cis*- and *trans*-4-*t*-butylcyclohexyl bromide and *cis*-4-methylcyclohexyl bromide.

cis-4-*t*-Butylcyclohexyl bromide was prepared from pure *trans*-4-*t*-butylcyclohexanol—readily available by reduction of the corresponding ketone with lithium aluminum hydride—aluminum chloride, followed by equilibration with acetone[4]— by treatment with phosphorus pentabromide.[5] This reaction produced, in addition to the desired *cis*-bromide, a minor amount of at least one isomeric bromide, possibly a 3-*t*-butylcyclohexyl bromide, as well as a substantial quantity of dibromide. The nature of the dibromide is discussed further below.

From the preparative point of view it was also satisfactory to prepare *cis*-4-*t*-butylcyclohexyl bromide from the commercially available mixed 4-*t*-butylcyclohexanols (containing about 80% of the *trans* isomer). In this case, 4-*t*-butylcyclohexene and *trans*-4-*t*-butylcyclohexyl bromide were additional contaminants of the desired product (having presumably originated from the *cis* alcohol). The crude monobromide was obtained from the mixed alcohol in 27% yield and was purified by repeated low-temperature recrystallization from pentane with a 32% recovery of the pure, crystalline *cis* isomer.

The presumed 3-*t*-butylcyclohexyl bromide contaminant was shown not to be a product of ring contraction, since hydrogenation of a mixture rich in this product, using Raney nickel in base as

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[1] (a) Presented in part before the Division of Organic Chemistry at the San Francisco meeting of the American Chemical Society, April 15, 1958. (b) Paper IV: E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5995 (1957).

[2] E. L. Eliel and R. G. Haber, *Chem. & Ind.* (*London*), 264 (1958); in connection with this problem *cf.* also ref. 3.

[3] P. Klaeboe, J. J. Lothe, and K. Lunde, *Acta Chem. Scand.*, **11**, 1677 (1957).

[4] M. Rerick and E. L. Eliel, Abstracts, San Francisco Natl. Meeting, Am. Chem. Soc., 4N (1958).

[5] Regarding the preparation of cyclohexyl halides from the alcohols and its steric course, *cf.* (a) R. J. Bridgewater and C. W. Shoppee, *J. Chem. Soc.*, 1709 (1953); (b) W. Hückel and H. Pietrzok, *Ann.*, **540**, 250 (1939); (c) M. Mousseron, R. Granger, and J. Valette, *Bull. soc. chim. France*, 244 (1946); (d) see also E. L. Eliel in M. Newman's "Steric Effects in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1956, pp. 128–130.

catalyst, gave *t*-butylcyclohexane. The 3-*t*-butylcyclohexyl bromide may have originated from 4-*t*-butylcyclohexene by addition of hydrogen bromide in the reaction mixture. This hypothesis appears unattractive, however, since pure *trans*-4-*t*-butylcyclohexanol gave the isomeric bromide, even though it gave almost no olefin; whereas the *cis* isomer, which gave much olefin, yielded almost none of the isomeric bromide. More likely, the 3-bromide resulted from a carbonium ion type rearrangement observed also in other conversions of alcohols to halides with phosphorus pentahalide.[5c,6] The characteristic infrared band of this bromide at 14.7μ as well as its stability to base suggested that it was an equatorial bromide, as might be expected to result from a carbonium ion,[7] whereas addition of hydrogen bromide to an olefin would more likely have yielded an axial bromide as the main product.[8] A weak band at 15.4μ suggests that traces of the axial isomer may have been formed also.

Other methods of synthesis of *cis*-4-*t*-butylcyclohexyl bromide were examined. Reaction of *trans* rich, commercial 4-*t*-butylcyclohexanol with phosphorus tribromide gave an olefin fraction and (in poor yield) a monobromide fraction. In this case no dibromide resulted, but appreciable amounts of phosphite ester were formed. This ester could be pyrolyzed to a mixture of *t*-butylcyclohexene isomers with the 4-*t*-butyl compound predominating. Treatment of the *trans* rich alcohol with 48% hydrobromic acid at reflux produced a monobromide fraction in high yield, but from infrared evidence, this material was a mixture of not only *cis*- and *trans*-4-*t*-butylcyclohexyl bromide but probably two other compounds (3-*t*-butylcyclohexyl bromides?) in such proportions that separation appeared quite unpromising.[9] No reaction took place when gaseous hydrogen bromide was passed through a pentane solution of the alcohol at 0°.

cis-4-Methylcyclohexyl bromide was synthesized, similarly as the 4-*t*-butyl homolog, from *trans*-4-methylcyclohexanol[10] and phosphorus pentabromide. The bromide obtained from it was again separated, by distillation into a monobromide fraction and a dibromide fraction. The monobromide appeared to be a mixture of *cis*-4-methylcyclohexyl bromide and an isomer, possibly a 3-bromide, which latter could be removed by low-temperature crystallization. The dibromide fraction in this case was not examined.

Impure *trans*-4-*t*-butylcyclohexyl bromide was obtained in only 8% yield from the relatively inaccessible pure *cis*-4-*t*-butylcyclohexanol[11] and phosphorus pentabromide. The crude monobromide fraction contained a little *cis* isomer and traces of the third bromide previously described. These traces may have been formed by the addition of hydrogen bromide to the olefin by-product. The dibromide fraction (main product) is discussed further below. There was also obtained, in this case, a substantial amount of olefin which, according to infrared spectrum, was a mixture of 1-, 3- and 4-*t*-butylcyclohexene.[12] It was not established whether the 1- and 3-*t*-butylcyclohexenes were rearrangement products of 4-*t*-butylcyclohexene formed initially by diaxial elimination, or whether they were primary rearrangement products formed directly from the alcohol by a carbonium-type rearrangement.

Because of the low yield in the above-described preparation of *trans*-4-*t*-butylcyclohexyl bromide, alternative routes to this compound were sought. *cis*-4-*t*-Butylcyclohexyl tosylate[13,1b] was treated with lithium bromide in acetone.[14] Not unexpectedly,[14] this led to much 4-*t*-butylcyclohexene, but, in addition, the desired *trans*-4-*t*-butylcyclohexyl bromide was contaminated with condensation products of acetone, which proved to be hard to remove, as well as with a small amount of *cis* isomer, probably resulting from inversion of the *trans* bromide by lithium bromide. An attempted inversion of *cis*-4-*t*-butylcyclohexyl bromide to the *trans* isomer with lithium bromide in acetone was even less promising, for the reaction was extremely slow and in addition to much unreacted starting material and acetone condensation products there was obtained not only the desired *trans*-4-*t*-butylcyclohexyl bromide but also the previously encountered third bromide (3-isomer?) which seemed impossible to remove.

Finally a method was developed which, though not affording much higher yields, employed a starting material more readily available than *cis*-4-*t*-butylcyclohexanol. 4-*t*-Butylbenzoic acid was hy-

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(6) *Cf.* W. Hückel and K. Kummerle, *Ber.*, **75**, 115 (1942); L. H. Darling, A. K. Macbeth, and J. A. Mills, *J. Chem. Soc.*, 1364 (1953); R. Cornubert and K. Nadjme-Abadi, *Compt. rend.*, **241**, 7 (1955); N. D. Zelinsky and K. A. Kozeschkov, *Ber.*, **60**, 1104 (1927); L. Palfray and B. Rothstein, *Compt. rend.*, **190**, 942 (1929).

(7) *Cf.* W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954).

(8) *Cf.* G. H. Alt and D. H. R. Barton, *J. Chem. Soc.*, 4284 (1954).

(9) We have been quite unsuccessful in separating any of these bromides by column chromatography on alumina. Low-activity alumina failed to give separation, high-activity alumina led to dehydrohalogenation.

(10) E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **23**, 2041 (1958).

(11) E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5992 (1957).

(12) The spectrum of pure 4-*t*-butylcyclohexene was recorded on a sample kindly supplied by Prof. Saul Winstein; *cf.* Ref. 13. The infrared spectra of pure 1- and 3-*t*-butylcyclohexene were taken from the thesis of Richard L. Reeves, University of Wisconsin, Madison, Wis. We thank Prof. Harlan L. Goering for making this thesis available to us. *Cf.* also H. L. Goering, R. L. Reeves, and H. H. Espy, *J. Am. Chem. Soc.*, **78**, 4926 (1956).

(13) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

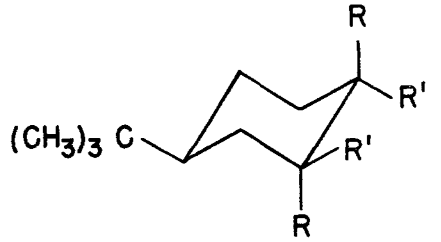
(14) S. Winstein, D. Darwish, and N. J. Holness, *J. Am. Chem. Soc.*, **78**, 2915 (1956).

drogenated to the corresponding cyclohexanecarboxylic acid (*cis* and *trans* isomer) which was subjected to the Hunsdiecker reaction.[15] A mixture of *cis*- and *trans*-4-*t*-butylcyclohexyl bromides rich in the *trans* isomer resulted here, and though it contained more of the *cis* contaminant than that obtained in the treatment of the *cis* alcohol with phosphorus pentabromide, both samples of the *trans* bromide could be purified by preferential destruction of the *cis* isomer with mineral base.[13]

Structural confirmations. The structure and configuration of the above-described *cis*-4-*t*-butylcyclohexyl bromide was confirmed by reaction with sodium thiophenolate. This led to a mixture of 4-*t*-butylcyclohexene and *trans*-4-*t*-butylcyclohexyl phenyl thioether, identical in infrared spectrum with an authentic sample.[1b] Since the thiophenolate reaction followed second-order kinetics,[2] application of Ingold's S_N2 rule[16] allows one to conclude that the starting *t*-butylcyclohexyl bromide was the *cis*-4 isomer. The structure and configuration of *cis*-4-methylcyclohexyl bromide was assigned by analogy and is in accordance with kinetic results, to be published later, which indicate that in the rate of its reaction with thiophenolate, *cis*-4-methylcyclohexyl bromide was intermediate between *cis*-4-butylcyclohexyl bromide and cyclohexyl bromide itself. The structure and configuration of *trans*-4-*t*-butylcyclohexyl bromide was deduced from the fact that it produced *cis*-4-*t*-butylcyclohexyl phenyl thioether,[1b] in addition to some 4-*t*-butylcyclohexene, upon prolonged boiling with alcoholic sodium thiophenolate.

The mixture of 1-, 3-, and 4-*t*-butylcyclohexenes mentioned earlier was subjected to catalytic hydrogenation. The mass spectrum and infrared spectrum of the resulting product indicated it to be mainly *t*-butyclyclohexane, by comparison with authentic spectra (API). A characteristic contaminant was 1-*t*-butylcyclohexene,[12] a not unexpected result, since this olefin, for steric reasons, should be hydrogenated more slowly than its 3- and 4-isomers.

The dibromides. The dibromide "A" obtained from *cis*-4-*t*-butylcyclohexanol with phosphorus pentabromide appeared to be a homogeneous substance, crystalline at low temperatures, and showed only two well-shaped carbon-bromine stretching bands in the infrared spectrum at 14.85 and 15.5μ. In contrast, the dibromide obtained similarly from *trans*-4-*t*-butylcyclohexanol appeared to be a mixture of at least two isomers. The major component "B" had C—Br stretching bands at 14.3 and 14.7μ, but there were also minor bands at 14.85 and 15.5μ which could be attributed to the above-described isomer A. Both dibromides were shown to be 3,4-dibromo-1-*t*-butylcyclohexanes on the basis of elementary analysis and the fact that both were dehalogenated in a variety of ways to 4-*t*-butylcyclohexene. Moreover, a mixture of the two bromides A and B was obtained by addition of bromine to 4-*t*-butylcyclohexene. Since A predominated in this bromine addition product, it is likely that A is the diaxial dibromide, *trans*-3-*cis*-4-dibromo-*t*-butylcyclohexane (I) whereas B is the diequatorial dibromide, *cis*-3-*trans*-4-*t*-butylcyclohexane (II); for it has been found[8] in the steroid series that addition of bromine to cyclohexenes gives predominantly the diaxial bromine addition product with minor amounts of the diequatorial isomer.



I. R = Br, R′ = H   II. R = H, R′ = Br

The configurational assignment of the dibromides is in agreement with the infrared spectral evidence (discussed further below) and the fact that the presumed diaxial dibromide A, upon prolonged heating by itself or in boiling alcohol solution was converted to a mixture of A and B. Interconversion of epimeric diaxial and diequatorial vicinal *trans* dihalides by heating has already been demonstrated in the steroid series,[8,17] whereas there is no precedent for the interconversion of a *cis*-(equatorial-axial)dibromide with either of its *trans* epimers. The fact that B had a higher boiling point than A is also in agreement with the assigned configurations II and I, inasmuch as II undoubtedly has the higher dipole moment and the Dipole Rule[18] predicts that the isomer of higher dipole moment should have the higher boiling point.

Several attempts were made to put the configurational assignment of A and B as I and II, respectively, on a firmer basis and, at the same time, to obtain a pure sample of the isomer B. These attempts were based on the following known facts: (1) Potassium iodide dehalogenates diaxial *trans* dihalides more rapidly than either diequatorial

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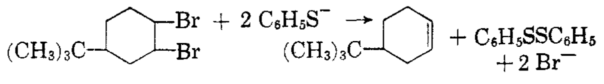
[15] *Cf.* E. L. Eliel and R. V. Acharya, *J. Org. Chem.*, **24**, 151 (1959).

[16] C. K. Ingold, ***Structure and Mechanism in Organic Chemistry***, Cornell University Press, Ithaca, N. Y., 1953, Chapter VII.

[17] In the steroid cases which have been studied, the equilibrium is almost entirely on the side of the diequatorial dibromide, whereas in the present case this is evidently not so. The difference is readily explained by the presence of the angular methyl groups at C_{10} in the steroids. This crowds the axial bromine substituent at C_2, C_4, or C_6 and forces the equilibrium all the way over to the diequatorial side. *Cf.* D. H. R. Barton and A. J. Head, *J. Chem. Soc.*, 932 (1956).

[18] N. L. Allinger, *J. Am. Chem. Soc.*, **79**, 3443 (1957). The rule has usually been applied to olefins but may apply to alicyclic diastereoisomers as well.

trans dihalides[8,19a] or equatorial-axial *cis* dihalides.[19b] (2) Axial halides suffer elimination with base more readily than equatorial halides.[13,20] (3) Axial bromine is more easily displaced by thiophenolate than is equatorial bromine.[2] Unfortunately, none of these attempts was very successful. Treatment of mixtures of A and B (as obtained from *trans*-4-*t*-butylcyclohexanol and phosphorus pentabromide) with potassium iodide in boiling ethanol for a short time produced enrichment of B in the residual dibromide. When the reaction time was extended, however, almost complete conversion of both A and B to 4-*t*-butylcyclohexene occurred. This is probably due to the relatively rapid interconversion of A and B, which would cause the presumed diequatorial dibromide B to be transformed to the presumed diaxial isomer A which would then be dehalogenated.[21] Treatment of the mixture of A and B with alcoholic sodium hydroxide produced a complex mixture in which B appeared to be somewhat enriched, but which still contained unchanged A in addition to a number of other components. Finally, sodium thiophenolate unexpectedly reacted with the mixture of A and B at room temperature to produce 4-*t*-butylcyclohexene and diphenyl disulfide, according to the equation



A search of the literature revealed that similar reactions of vicinal dihalides have been described many years ago.[22a] The reaction seems to show little discrimination between diequatorial and diaxial isomers—being, in this respect, similar to the zinc dehalogenation[22b]—since both A and B were dehalogenated readily at room temperature. The stereochemical aspect of this reaction merits further investigation.

Infrared spectra. The frequencies of absorption in the infrared region (in cm.$^{-1}$) due to the C—Br stretching motion for the compounds here prepared and some related ones are listed in Table I.

TABLE I

INFRARED FREQUENCIES DUE TO C—BR STRETCHING

Compound	Peak	
	Axial	Equatorial
cis-4-*t*-Butylcyclohexyl bromide	670	. . .
trans-4-*t*-Butylcyclohexyl bromide	. . .	692
cis-4-Methylcyclohexyl bromide	684	708
Cyclohexyl bromide	685	709
trans-4-*cis*-3-Dibromo-*t*-butylcyclohexane	. . .	680, 699
cis-4-*trans*-3-Dibromo-*t*-butylcyclohexane	646, 672	. . .
trans-1,2-Dibromocyclohexane[8]	663	684, 693

The equatorial bands are in the 690–710 cm.$^{-1}$ region with a second band at slightly lower frequency in the diequatorial dibromides. The axial bands fall in the 670–685 cm.$^{-1}$ region with a splitting and shift to lower frequencies in the dibromides. This conclusion is generally similar to that reached by Barton[23] from examination of a series of steroidal bromides. It might be noted, however, that our equatorial bromides lie near the lower end of the frequency region (682–833 cm.$^{-1}$) given by Barton whereas our axial bromides absorb near the upper end of his frequency range (542–692 cm.$^{-1}$). Moroever, the shift in frequency in our diaxial dibromide (from 670–685 cm.$^{-1}$ to 646 and 672 cm.$^{-1}$) is much less than the shift in the steroids where the diaxial dibromides absorb around 550 cm.$^{-1}$ [24]

DISCUSSION

The major monobromide products obtained by treatment of *cis*- and *trans*-4-*t*-butylcyclohexanol with phosphorus pentabromide have configurations opposite to those of the starting materials. This is in agreement with the steric course of the reaction of cholestanol and epicholestanol with phosphorus pentahalides.[5a] In contrast, treatment of the alcohols with hydrogen bromide gives complex mixtures of positional as well as configurational isomers, in contradistinction to what has been reported in the 3-methylcyclohexanol series.[5c,5d,25]

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(19) (a) D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951). (b) H. L. Goering and H. H. Espy, *J. Am. Chem. Soc.*, **77**, 5023 (1955).

(20) H. L. Goering and H. H. Espy, *J. Am. Chem. Soc.*, **78**, 1454 (1956).

(21) Unfortunately, we were not able to demonstrate that the presumed diequatorial isomer B is converted to a mixture of A and B by heating. It appears that the mixtures of A and B which we obtained by action of phosphorus pentabromide on *trans*-4-*t*-butylcyclohexanol were so close to the presumed equilibrium mixture that heating them produced no appreciable change in composition. However, if thermal conversion of A to an A-B mixture is indeed equilibration, as appears highly likely, the equilibrium must also be approachable from the side of pure B and at about the same rate as it is approached from pure A; for the equilibrium mixture contains appreciable amounts of *both* isomers, *i.e.*, *K* is not too far from unity.

(22) (a) R. Otto, *J. prakt. Chem.*, [2], **51**, 299 (1895). Elimination seems to occur with all vicinal dibromides more highly branched than ethylene or propylene bromide (which undergo substitution only); *cf.* also J. Hine and W. H. Brader, *J. Am. Chem. Soc.*, **75**, 3964 (1953). This reaction, to which little attention has been paid, may be quite useful from the preparative point of view. (b) *cf.* D. R. James, R. W. Rees, and C. W. Shoppee, *J. Chem. Soc.*, 1370 (1955).

(23) D. H. R. Barton, *Experientia suppl.*, II, 121 (1955); see also D. H. R. Barton, J. E. Page, and C. W. Shoppee, *J. Chem. Soc.*, 331 (1956).

(24) With our instrument we could not observe the spectra below 625 cm. However, there is little doubt that our bands at 646 and 672 cm.$^{-1}$ correspond to the steroidal bands at 542 and 548 cm.$^{-1}$

(25) M. Mousseron and R. Jacquier, *Bull. soc. chim. France*, 80C (1951). We are somewhat at a loss to understand how these investigators were able to reach definite conclusions as to the identity of the 3-methylcyclohexyl bromides without the benefit of infrared spectroscopy.

Not unexpectedly,[26] olefins are obtained as major by-products in the reaction of the (axial) *cis*-alcohol, but not of the (equatorial) *trans*-alcohol.

The formation of major amounts of vicinal dibromides in the treatment of both *cis*- and *trans*-4-*t*-butylcyclohexanol with phosphorus pentabromide, though at first sight surprising, is in agreement with observations of other investigators for this reagent[5a] as well as for phosphorus pentachloride.[5b,27] Goering and McCarron[27] have shown that the formation of a vicinal dichloride from 3,3-dimethylcyclohexanol does not involve the olefin as an intermediate, for optically active alcohol gives active dichloride whereas both possible olefin intermediates are symmetrical. Our results corroborate this point, for if 4-*t*-butylcyclohexene were an intermediate in the conversion of *cis*- and *trans*-4-*t*-butylcyclohexanol to 3,4-dibromo-*t*-butylcyclohexanes, the two epimeric alcohols should give rise to the same dibromide (or dibromide mixture), whereas in fact they do not. It has been proposed[27,28] that the reaction leading to the dihalide proceeds *via* an alkoxyphosphorus tetrahalide, π-complex of a carbonium ion, and π-complex of a halonium ion as shown in Figure 1.

This reaction scheme may be readily applied to *cis*-4-*t*-butylcyclohexanol where—assuming diaxial ring opening[28,29] in the last step—the predicted product is the diaxial dibromide, as actually found. It is more difficult to see how the π-complex can be formed from *trans*-4-*t*-butylcyclohexanol (equatorial hydroxyl) in view of the requirement[8] that a neighboring group must be *conformationally trans* to the functional substituent in whose reaction it participates. On this basis, *trans*-4-*t*-butylcyclohexanol is properly disposed for ring contraction (which does not, however, occur) but not for participation of an adjacent hydrogen. Possibly the molecule may flip over into the conformation in which hydroxyl (or the —$OPBr_4$ grouping) is axial. In this conformation, the system is stereoelectronically disposed for the same sequence of events described above for the *cis*- alcohol (Fig. 1). This sequence would eventually lead to a diaxial dibromide which could then flip back to the observed diequatorial product. However, if in the course of this reaction sequence either the *t*-butyl group has to become axial or the ring has to become boat-shaped (*cf.* Fig. 2) the activation energy for the process would be improbably high. Perhaps the molecule can distort itself sufficiently to allow the course of events shown in Fig. 1 to happen without completely taking up the unfavorable conformations shown in Fig. 2. This would involve some intermediate conformation in the transition state where neither the —$OPBr_4$ grouping nor the *t*-butyl group are *completely* axial. It may or may not be significant that dibromide formation from the *trans* alcohol appears to be less stereospecific than that from the *cis* alcohol in that it leads to two diastereoisomeric products.[30]

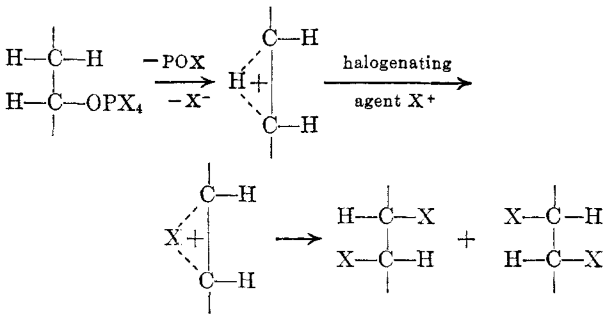

Figure 1

EXPERIMENTAL[31]

cis-4-t-Butylcyclohexyl bromide. From commercial 4-t-butylcyclohexanol and phosphorus pentabromide. Ninety g. of bromine dissolved in 100 ml. of methylene chloride was slowly added to a cooled (ice bath) solution of 150 g. of phosphorus tribromide, in 150 ml. of methylene chloride, with stirring. A yellow precipitate was formed. Seventy-seven g. of commercial 4-*t*-butylcyclohexanol (about 80% *trans* isomer), dissolved in the minimum amount of methylene chloride, was slowly added to the cooled and well-stirred mixture. The addition was completed in 1 hr. but stirring was continued for 3 hr. more, resulting in evolution of hydrogen bromide. Ice water (500 g.) was then added and stirring continued for an additional hour to decompose the phosphorus halides. After separating the layers, the organic phase was washed with water, sodium bicarbonate solution, and brine. After stripping the dried methylene chloride, the residue was distilled through a 12-in. helix-packed column under reduced pressure. The first fraction (a few drops) distilled at 57–65°/14 mm. and consisted mainly of 4-*t*-butylcyclohexene (infrared spectrum).

The second fraction distilled at 104–110°/14 mm. and constituted a *t*-butylcyclohexyl bromide mixture. After a small intermediate fraction another compound came over at 142°/15 mm. It was shown to be a mixture of 4-*t*-butylcyclohexyl dibromides. Fraction 2 (30 g.) was recrystallized nine times from pentane between room temperature and −70°. *cis*-4-*t*-Butylcyclohexyl bromide (9.3 g.), m.p. 23–25°, b.p. 70°/2 mm. n_D^{20} 1.4912 (supercooled liquid) was obtained. The characteristic infrared bands (neat supercooled liquid)

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(26) (a) D. H. R. Barton, *Experientia*, **6**, 316 (1950); (b) See also D. H. R. Barton and R. Cookson, *Quart. Revs.*, **10**, 44 (1956).

(27) H. L. Goering and F. H. McCarron, *J. Am. Chem. Soc.*, **78**, 2270 (1956).

(28) *Cf.* G. A. Russel and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4025 (1955).

(29) Ref. 5d, pp. 130–134.

(30) The significance of this fact may be impaired because (a) diaxial dibromide from equatorial alcohol may result through a mechanistically distinct path, *viz.* addition of free bromine to 4-*t*-butylcyclohexene; (b) some of the diaxial dibromide may have originated through isomerization of the diequatorial isomer during fractionation (*vide supra*). This seems less likely, since the diaxial dibromide can be obtained quite free of the diequatorial isomer by distillation, even though it, also, is not stable to prolonged heating.

(31) Infrared analyses on a Baird double-beam instrument by Mr. Rolland S. Ro and the authors. Mass spectral analysis by Mr. George Young. Microanalyses by Midwest Microlab, Indianapolis, Ind., and Mr. Josef Nemeth, Urbana, Ill.

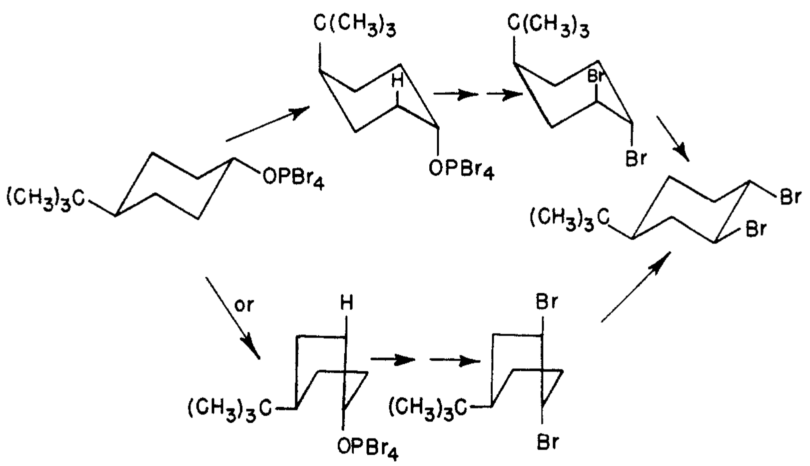

Fig. 2

of this compound (not shared by the *trans* isomer) were at 6.91, 6.97, 7.60, 7.95, 8.05, 9.28, 9.75, 10.87, 11.03, 11.65, 11.97, and 14.92μ.

Anal. Calcd. for $C_{10}H_{19}Br$: C, 54.79; H, 8.74; Br, 36.46. Found: C, 54.72; H, 8.61; Br, 36.54.

The dibromide fraction was chromatographed on alumina from pentane to remove traces of oxygenated impurities and then redistilled, a fraction boiling at 116–124°/5 mm., n_D^{23} 1.5251 being submitted for analysis.

Anal. Calcd. for $C_{10}H_{18}Br_2$: Br, 53.62. Found: Br, 53.53.

This dibromide, to which the *cis*-3-*trans*-4-dibromo-*t*-butylcyclohexane structure was assigned, had characteristic infrared bands at 7.72, 8.65, 8.87, 10.12, 10.34, 11.21, 12.35 (prominent), 14.3, and 14.7μ. The analytical sample had in addition, however, a number of the characteristic bands of the diaxial (*trans*-3-*cis*-4-) isomer (*vide infra*). The sample was not changed in infrared spectrum by six hours heating at 125–130°.

From pure trans-4-t-butylcyclohexanol and phosphorus pentabromide. Forty-one g. of *trans*-4-*t*-butylcyclohexanol prepared by the reduction of the ketone with mixed hydride[4] were treated with phosphorus pentabromide prepared *in situ* from 110 g. of phosphorus tribromide and 55 g. of bromine, as described above. After the same work-up, a monobromide was obtained whose I.R. spectrum showed it to be *cis*-4-*t*-butylcyclohexyl bromide contaminated with the third bromide (I.R. bands at 13.2, 14.7, and 15.4μ.) There was no indication for the presence of *trans*-4-*t*-butylcyclohexyl bromide. Again a very small amount of olefin was obtained in the first distillation fraction. A dibromide fraction boiling at 142°/15 mm. consisted mainly of the diequatorial dibromide but contained also some of the diaxial isomer.

From commercial 4-t-butylcyclohexanol and phosphorus tribromide. Commercial 4-*t*-butylcyclohexanol (10.9 g.) was dissolved in 50 ml. of benzene. Phosphorus tribromide (25 ml.) was slowly added (stirring) and the mixture then refluxed for 1 hr. A yellow precipitate formed on boiling. The mixture was cooled in an ice bath and ice water added. The benzene layer was separated and washed with water, bicarbonate solution, and brine. The bicarbonate washing produced a white (acid soluble) precipitate which was filtered off. The dried organic solution was stripped leaving a yellow oil (5.9 g.) which, on distillation yielded four fractions:

Fraction 1, b.p. 60–100°/15 mm.—mainly 4-*t*-butylcyclohexene and its isomers.

Fractions 2 and 3, b.p. 100–104°/15 mm.—monobromide fraction (4 g.).

After this, at a pot temperature of 230°, pyrolysis of the residue occured, giving again 4-*t*-butylcyclohexene and its isomers.

Fractions 2 and 3 were identical in I.R. spectrum and consisted of *cis*-4-*t*-butylcyclohexyl bromide, the *trans* isomer and the third bromide. The pure *cis* isomer could be obtained by repeated crystallization from pentane at −70°.

From commercial 4-t-butylcyclohexanol and phosphorus tribromide under varied conditions. (a) One g. of the above alcohol was dissolved in 5 ml. of pyridine, and 0.4 ml. phosphorus tribromide was added. A yellow precipitate formed immediately. The mixture was left at room temperature.

(b) One g. of the alcohol was dissolved in 5 ml. chloroform, and 1 g. anhydrous calcium carbonate and 0.4 ml. of phosphorus tribromide were added. The mixture was left at room temperature.

(c) One g. of the alcohol was dissolved in 4.5 ml. of benzene, and 0.4 ml. of phosphorus tribromide was added at room temperature.

After 9 hr. samples of the three reaction mixtures were withdrawn, poured into water, extracted with pentane, dried and concentrated. The product of reaction (a) was a solid. The products from reactions (b) and (c) were liquids and contained bromides but many bands indicating phosphorus were seen in the I.R. spectrum, at 4.15 (P—H), 7.95 (P=O), 8.95, 9.5 (C—O—P), 10.3, and 12.43μ.

After 3 days the reactions were worked up as above except that methylene chloride was used as the organic solvent. The crude yield from (a) was 0.70 g., (b) 0.86 g., (c) 0.86 g. Each of the products was percolated through a small alumina (Merck 20 g.) column to eliminate phosphorus esters. The yield after that: (a) 0.05 g., (b) 0.36 g., (c) 0.42 g. The infrared spectra showed (a) not to contain any of the desired bromide; (b) contained at least three bromides; (c) as (b) except that the band at 14.7μ (of the third bromide) was weaker. These tests were considered unpromising.

The reaction of commercial 4-t-butylcyclohexanol and hydrogen bromide. Commercial 4-*t*-butylcyclohexanol (5.4 g.) was boiled with 35 ml. hydrobromic acid (48%) in a flask connected through a 10-in. Vigreux column to a distillation apparatus. Slow distillation was permitted to occur and continued till all organic material distilled over. Water was added to the distillate, the layers were separated, and the aqueous layer was extracted with pentane. The combined organic extracts were washed, dried, and stripped. The residue was distilled. After a very small forerun the bulk of the material distilled at 104°/15 mm., n_D^{20} 1.4908. Yield almost quantitative. The bromide so obtained contained both the *cis*- and the *trans*-4-*t*-butylcyclohexyl bromide as seen from the infrared spectrum. The *trans* isomer seemed to predominate. However strong extraneous bands were found at 7.98, 8.88, 9.45, 10.20, 11.80, 12.40, 13.30, 14.72, and 15.40μ. By treating this mixture with alcoholic base the *cis*-4-*t*-butylcyclohexyl bromide could be selectively destroyed (infrared evidence). However the other extraneous bromide survived. Chromatography over alumina (Merck, acid washed), 100-1, using pentane as solvent did not lead to appreciable separation. Using alumina (Woelm) activity I, neutral, acid, or basic, only olefins (the three isomeric *t*-butylcyclohexenes) came off the column, even after periods as short as 15 min.

Using a starting material containing the two stereoisomeric alcohols in almost identical proportions (50:50) the reaction product seemed to consist of the same mixture as above.

trans-4-t-Butylcyclohexyl bromide. From cis-4-t-butylcyclohexanol and phosphorus pentabromide. Seventy-four g. of *cis*-4-*t*-butylcyclohexanol[11] was treated with phosphorus pentabromide prepared from 135 g. phosphorus tribromide and 80 g. bromine in the same way as described for its isomer. The residue after work-up was distilled under reduced pressure. Fraction 1, b.p. 55–56°/13 mm. consisted mainly of 4-*t*-butylcyclohexene contaminated with its two isomers as evidenced by bands at 7.85, 9.63, 11.90, 12.50 (1-*t*-butylcyclohexene) and bands at 8.80, 11.25, 11.60, 13.10, and 13.85μ (3-*t*-butylcyclohexene).[12]

Fraction 2 was an intermediate fraction (b.p. 58–103°/13 mm.).

Fraction 3, b.p. 103–105°/13 mm. and fraction 4, b.p. 105–108°/13 mm. consisted of *trans*-4-*t*-butylcyclohexyl bromide contaminated with a little *cis* isomer and a trace of the third isomer. It appears that fraction 4 was slightly purer than fraction 3.

Fraction 5, b.p. 108–142°/13 mm. consisted mainly of dibromide.

Fractions 3 and 4 were combined and redistilled. Eight g. of middle cut, b.p. 104–107/13 mm. was obtained and further purified as explained below.

Fraction 5 was redistilled and a middle cut was collected at 142°/13 mm. This was the main product of the reaction and consisted of a dibromide which crystallized from pentane at −70°.

Anal. Calcd. for $C_{10}H_{18}Br_2$: Br, 53.62. Found: 53.57.

This dibromide seems to be *trans*-3-*cis*-4-dibromo-*t*-butylcyclohexane. Characteristic infrared bands are found at 8.82, 9.67, 11.81, 14.9, and 15.5μ. The characteristic bands of the diequatorial (*cis*-3-*trans*-4) isomer (*vide supra*) were absent. After 6 hr. heating at 125–130°, the infrared spectrum of the material had changed considerably and now resembled closely that of the (impure) *cis*-3-*trans*-4-isomer described above. A similar change in spectrum was observed when the dibromide was boiled for 3 days in 90% ethanol solution.

From 4-t-Butylcyclohexanecarboxylic acid. p-t-Butylbenzoic acid was hydrogenated and the product submitted to a Hunsdiecker reaction.[15] The product so obtained consisted of a mixture of only the two 4-*t*-butylcyclohexyl bromides with the *trans*-isomer predominating.

Purification of trans-4-t-Butylcyclohexyl Bromide. The crude bromide obtained by the Hunsdiecker reaction (9.1 g.) was boiled with 0.4 g. potassium hydroxide in 25 ml. ethanol for 13 hr. The reaction mixture was poured into water and extracted with pentane. The organic extracts were washed with 20% calcium chloride solution, dried, and stripped. Most of the *cis* isomer had been dehydrobrominated. To this crude residue was added 8 g. of the bromide obtained from *cis*-4-*t*-butylcyclohexanol and together they were boiled with 0.4 g. potassium hydroxide in 35 ml. ethanol for another 13 hr. The product was worked up as above. The olefin formed was separated from the bromide by distillation. Nine g. of essentially pure *trans* bromide was obtained. This sample was percolated through alumina (Merck, acid washed) in pentane, to remove possible traces of ethers, recrystallized once from pentane at −70° and distilled at 120°/24 mm. ($n_D^{20.2}$ 1.4868). It had infrared bands at 7.85, 8.55, 9.10, 9.62, 11.1, 11.4, 12.25, and 14.45μ. The characteristic bands of the *cis*-isomer and the third compound (above) were absent.

Anal. Calcd. for $C_{10}H_{19}Br$: C, 54.79; H, 8.74; Br, 36.46. Found: C, 55.02; H, 8.93; Br, 36.17.

cis-4-Methylcyclohexyl Bromide. Seventy-two g. of *trans*-4-methylcyclohexanol[10] b.p. 172.6–173°/734 mm., was treated with phosphorus pentabromide prepared *in situ* from 170 g. phosphorus tribromide and 100 g. bromine in the same manner as described above. After the usual work-up, the product was distilled. No olefin was detected. Fraction 1, b.p. 64–65°/14 mm., 22.9 g., consisted mainly of *cis*-4-methylcyclohexyl bromide but extraneous bands at 7.98, 8.20, 9.53, 9.65, 9.92, 14.4, and 15.05μ were observed in the infrared spectrum.

Fraction 2 was a mixed fraction. Fraction 3, b.p. 64°/1.5 mm. consisted of dibromide(s?). Fraction 1 was recrystallized repeatedly from pentane at −70°, till all the above-mentioned extraneous infrared bands disappeared. It was then percolated through alumina and redistilled. Yield 9.5 g. Characteristic infrared bands at 14.11 and 14.6μ.

Anal. Calcd. for $C_7H_{13}Br$: C, 47.46; H, 7.40; Br, 45.12. Found: C, 47.44; 47.29; H, 7.45; Br, 44.66.

Reaction of cis-4-t-Butylcyclohexyl Bromide with Sodium Thiophenolate. cis-4-*t*-Butylcyclohexyl bromide (1.85 g.) was added to a solution of 0.21 g. sodium and 1.1 g. thiophenol in 10 ml. methanol. The mixture was refluxed for 36 hr. under nitrogen. Most of the methanol was then distilled *in vacuo* and the residue poured into water and extracted with ether. The organic layer was washed with sodium hydroxide solution, dilute acid, bicarbonate, and brine. The residue after stripping was distilled at 14 mm. Two fractions were collected. The first b.p. 65°/14 mm. consisted of pure 4-*t*-butylcyclohexene and the second, b.p. 185°/14 mm., was shown to be *trans*-4-*t*-butylcyclohexyl phenyl thioether, since its infrared spectrum was identical with that of an authentic sample[1b] and contained none of the bands of the *cis*-isomer.

Reaction of trans-4-t-butylcyclohexyl bromide with sodium thiophenolate. One-half g. of *trans*-4-*t*-butylcyclohexyl bromide was added to a solution of 0.1 g. sodium and 3 g. thiophenol in 40 ml. ethanol. The reaction mixture was kept on a steam bath for 3 days, under nitrogen. It was worked up as described for the *cis* isomer. This time, a little starting material had not yet reacted but again 4-*t*-butylcyclohexene had been formed. The *cis*-4-*t*-butylcyclohexyl phenyl thioether obtained had the same infrared spectrum as an authentic sample[1b] and no bands of its isomer were found.

Reaction of cis-4-t-butylcyclohexyl tosylate with lithium bromide.[14] *cis*-4-*t*-Butylcyclohexyl tosylate[1b,13] (6.16 g.) and 1.6 g. lithium bromide were dissolved in 50 ml. acetone (freshly distilled over potassium carbonate) and the mixture refluxed for 20 hr. The acetone was evaporated and the residue taken up in water and pentane. The organic layer was stripped and the residue distilled under reduced pressure. Four fractions were collected.

Fraction (a) b.p. 40–46°/17 mm., n_D 1.4500, was mesityl oxide.

Fraction (b) b.p. 52–60°/17 mm. was mainly 4-*t*-butylcyclohexene.

Fraction (c) b.p. 77–104°/17 mm. unidentified mixture.

Fraction (d) b.p. 104–108°/17 mm. consisted mainly of *trans*-4-*t*-butylcyclohexyl bromide contaminated with an olefinic ketone (infrared bands at 5.95, 6.03, 6.2, 8.2, 9.0, 9.18, 9.7, 11.5, and 12.9μ). It was chromatographed on an alumina (Merck acid washed) column using pentane as eluent. Most of the interfering ketone was removed. The infrared spectrum of this sample showed it to be *trans*-4-*t*-butylcyclohexyl bromide with traces of the *cis* isomer.

Reaction of cis-4-t-butylcyclohexyl bromide with lithium bromide. cis-4-*t*-Butylcyclohexyl bromide (1.3 g.) was refluxed with a saturated solution of lithium bromide in 20 ml. acetone for two days. The acetone was removed *in vacuo* and the residue taken up in pentane. The organic solution was washed with sodium bicarbonate soln., dried, and stripped. The infrared spectrum of the crude residue showed the presence of mesityl oxide, *trans*-4-*t*-butylcyclohexyl bromide and mainly starting material. The mixture was taken up in a fresh solution of lithium bromide in acetone and refluxed for 2 weeks. After the same work-up as above, the residue was distilled. The mesityl oxide came over first and no 4-*t*-butylcyclohexene was found. The bromide fraction was dissolved in pentane and chromatographed over alumina to remove acetone condensation products. The material so obtained still contained traces of ketone. It consisted of a mixture of *cis*- and *trans*-4-*t*-butylcyclohexyl bromide as well as the third bromide. The infrared spectrum of the material looked very much like that of the product obtained by boiling 4-*t*-butylcyclohexanol with hydrobromic acid.

Debromination of 3,4-dibromo-t-butylcyclohexane. With potassium iodide. 3,4-Dibromo-*t*-butylcyclohexane (27.2 g.), as obtained in the reaction of commercial 4-*t*-butylcyclohexanol with phosphorus pentabromide, and 37 g. potassium iodide were dissolved in 350 ml. 90% ethanol and refluxed for 6 hr. The alcoholic solution was poured into water and extracted repeatedly with pentane. The organic layer was washed with sodium thiosulfate solution, 20% calcium chloride soln., sodium bicarbonate soln., and brine. After drying over sodium sulfate the pentane was evaporated. The infrared spectrum of the residue showed that part of the dibromide had been converted to 4-*t*-butylcyclohexene and that the dibromide with C—Br 14.7 bands at 14.13 and 14.7μ had been enriched at the expense of the dibromide having C—Br bands at 14.85 and 15.5μ.

The crude residue was taken up in another solution of 20 g. potassium iodide in 300 ml. 90% ethanol and refluxed for 12 hr. after which the mixture was left standing at room temperature for 7 days. It was worked up as above. The infrared spectrum showed a further enrichment but the axial C—Br bands at 14.85 and 15.5μ were still present.

3,4-Dibromo-*t*-butylcyclohexane (14.4 g.), rich in the diequatorial isomer, was treated with a solution of 20 g. potassium iodide in 200 ml. 90% ethanol. The mixture was refluxed for 3 days. It was poured into water to which a slight excess of sodium thiosulfate had been added. The mixture was worked up as before and the residue distilled. Pure 4-*t*-butylcyclohexene (5.2 g.) was obtained. Later 1.5 g. of unreacted dibromide with a trace of olefin distilled over. The infrared spectrum showed the diequatorial dibromide to be the main component but the diaxial isomer was still present.

With zinc and acetic acid. A similar 3,4-dibromo-*t*-butylcyclohexane mixture as above (12.7 g.), was dissolved in 60 ml. acetic acid and small amounts of zinc powder were added in portions over a period of three hours. After that time a white precipitate was observed and the reaction was stopped by pouring the mixture into water. The mixture was extracted with pentane and worked up in the usual manner. The residue was distilled *in vacuo.* 4-*t*-Butylcyclohexene (2.3 g.) contaminated by its two position isomers was obtained. After that 3.0 g. of unreacted dibromide distilled over. It was enriched in the diequatorial isomer at least to the same extent as the product obtained by the potassium iodide reaction. The low yield of the olefin might be accounted for by its low boiling point and some of it might have been lost while evaporating the pentane.

With sodium thiophenolate. To a solution of 3.0 g. (0.01 mole) of 3,4-dibromo-*t*-butylcyclohexane, rich in the presumed diequatorial isomer, in 10 ml. 87% ethanol was added 2.75 g. (0.025 mole) of thiophenol and 20 ml. (0.022 mole) of a 1.1 N solution of base obtained by dissolving sodium in 87% ethanol. After four days at room temperature, a copious, beautifully crystalline precipitate had formed. This was collected and identified as diphenyl disulfide, m.p. 59.5–60.8° (lit. 61°), undepressed by admixture with authentic material, and weighed 1.6 g. (73%). The filtrate was poured into water, extracted with ether-petroleum ether and the extract washed with aqueous potassium hydroxide, water, aq. calcium chloride and dried over calcium chloride. The residue, after concentration, contained very little residual dibromide, according to infrared spectrum. Upon chromatography, most of the material was eluted with petroleum ether and the infrared spectrum did not change. Distillation of this material gave 4-*t*-butylcyclohexene, b.p. 68°/22 mm. (lit. 65–66°/20 mm.),[1b] identified by infrared spectrum, and further amounts of diphenyl disulfide.

Elimination of bromine from the diequatorial dibromide probably does not involve prior equilibration with the diaxial isomer since a control experiment showed that the diaxial isomer was unaffected by standing with 87% ethanol for four days.

Addition of bromine to 4-t-butylcyclohexene. Pure, freshly prepared,[32] 4-*t*-butylcyclohexene (5.2 g.) was dissolved in 20 ml. of chloroform and cooled to 0°. A solution of 6 g. bromine in 10 ml. of chloroform was slowly added with stirring. The solution turned cloudy. A preliminary experiment had shown that the addition does not stop after the calculated amount had been added so that no attempt was made to add bromine till the color of bromine persisted.

The organic solution was washed with water, bicarbonate, and brine. It was dried over potassium carbonate and stripped. The residue (10 g.) was distilled at 12 mm. Four fractions were collected.

Fraction 1 (few drops) contained unreacted olefin and traces of ketone. Fractions 2 and 3 contained the desired dibromide. This was a mixture of the two dibromides encountered before, with the diaxial predominating. Fraction 4 turned pink on distillation and its infrared spectrum had some extraneous bands; it probably contains more highly brominated material.

Hydrogenation of t-butylcyclohexene. The olefin mixture obtained from the reaction of pure *cis*-4-*t*-butylcyclohexanol with phosphorus pentabromide (3.7 g.) was hydrogenated over platinum oxide in alcohol. This olefin mixture contained mainly 4-*t*-butylcyclohexene but the infrared spectrum had shown extraneous bands at 13.85μ (3-*t*-butylcyclohexene); 12.50, 11.90, 9.62, 7.85μ (1-*t*-butylcyclohexene) and 13.10, 11.60, 11.25, and 8.80μ (both these isomers).

One mole of hydrogen was taken up. The catalyst was filtered off, the alcoholic solution poured into water and extracted with pentane. The pentane solution was washed with 20% calcium chloride solution, dried and stripped. The residue was distilled in a bulb-tube (70° air bath temp.; 13 mm. pressure) yielding 2.75 g. of a product of $n_D^{20.2}$ 1.4489. The infrared spectrum was compared with API spectrum 55° (*t*-butylcyclohexane n_D^{20} 1.4464). Extraneous bands were found at 7.83, 8.80, 10.50, 10.88, 11.61, 12.30, 13.1, and 14.33μ. All these could be assigned to 1-*t*-butylcyclohexene which must have escaped hydrogenation because of steric hindrance.

In another experiment, olefin mixtures obtained from the reaction of commercial 4-*t*-butylcyclohexanol and phosphorus pentabromide were hydrogenated as above. The olefin had strong extraneous bands at 13.08 and 14.32μ. After hydrogenation these extraneous bands persisted. The mass spectrum of this sample showed among others an extraneous peak at parent minus six. The infrared spectrum of *t*-butylbenzene was then consulted and indeed its strongest bands were at 13.08 and 14.32μ.

Hydrogenolysis of bromide mixtures. Ten g. of a mixture of *t*-butylcyclohexyl bromides as obtained from the reaction of 4-*t*-butylcyclohexanol and hydrobromic acid was treated with Raney nickel (one teaspoon) in 100 ml. 8% ethanolic potassium hydroxide and hydrogen (50 p.s.i) for 6 hr. The product was left standing in this solution for 2 weeks at room temperature and then worked up in the usual manner and distilled. The first and main fraction (65°/15 mm.) consisted of a mixture of *t*-butylcyclohexane and 4-*t*-butylcyclohexene. Only one band (9.0μ) could not be assigned to these compounds and probably represents a C—O band. The second, very minor, fraction was unreacted bromide. The *trans*-4-*t*-butylcyclohexyl bromide was preferably used up.

This reaction was repeated except that after the six hours hydrogenolysis the product was isolated immediately

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[32] On standing hydroxyperoxides are formed quite rapidly leading to undesired oxygen-containing impurities.

and rehydrogenated with platinum oxide as catalyst. The infrared spectrum (0.02 mm. neat film) of the product ($n_D^{20.2}$ 1.4479) was identical to *t*-butylcyclohexane except for an extraneous band at 9.0μ. An infrared spectrum in a 0.2 mm. cell revealed however also extraneous bands at 9.4, 13.1, and 14.3μ. These bands can be assigned to *t*-butylbenzene.

Reaction of a Mixture of 3-trans-4-cis- and 3-cis-4-trans-dibromo-t-butylcyclohexane with sodium hydroxide. The dibromide mixture obtained from the reaction of commercial 4-*t*-butylcyclohexanol and phosphorus pentabromide (24.1 g.), was treated with 50% of the calculated amount of sodium hydroxide in 200 ml. 85% ethanol. It was left standing at room temperature for 2 weeks. The alcoholic solution was then poured into water and extracted with pentane. The pentane solution was washed dried and stripped. Twenty g. of residue were obtained. The infrared spectrum of the crude residue showed that appreciable amounts of the diaxial isomer were still present. The crude residue was then boiled with a solution of 3 g. sodium hydroxide in 200 ml. ethanol for 3 hr. It was worked up as before and 15 g. of crude residue was obtained. The material was distilled at 15 mm.

Fraction 1, b.p. 64–90°; fraction 2, b.p. 90–99°; fraction 3, residue. Fraction 1 was an olefinic mixture with bands in the 9μ region and characteristic bands at 12.9, 13.1, 13.6, 14.9, and 15.4μ.

Fraction 2 was a different olefinic mixture with characteristic bands at 12.8, 13.8, and 15.03μ.

Fraction 3 (residue) was mainly diequatorial dibromide with some diaxial isomer and at least one further product, probably an ether. No further attempts were made to separate this complex mixture.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Conformational Analysis. VI. The Hunsdiecker Reaction with *cis*- and *trans*-4-*t*-Butylcyclohexanecarboxylic Acid[1]

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Reaction of the silver salts of *cis*- and *trans*-4-*t*-butylcyclohexanecarboxylic acid with bromine in boiling carbon tetrachloride gave identical mixtures of 4-*t*-butylcyclohexyl bromides containing 65 ± 3% of the *trans* isomer. Neither the *cis* acid nor the *cis*-bromide is appreciably epimerized under the conditions of the reaction.

The reaction of the silver salt of an organic acid with bromine to give an alkyl bromide, carbon dioxide, and silver bromide: $RCOOAg + Br_2 \rightarrow RBr + CO_2 + AgBr$ is generally known as the Hunsdiecker Reaction.[2] The likely mechanism of this reaction has been discussed extensively[2b-d-4] and it appears that a mechanism involving free radicals as intermediates best fits most of the known facts.[5]

Among the evidence favoring a free radical mechanism are optical studies in systems where the group R is asymmetric at its point of attachment to the carboxylate group.[3,6-10] In all but two[6,7] of these cases an active acid RCOOH gave rise to a racemic bromide R—Br, as is to be expected if the reaction proceeds *via* the radical R·.[11] Of the two remaining cases,[6,7] one,[6] the conversion of silver hydratropate $C_6H_5CH(CH_3)COOAg$ to α-phenethyl bromide, $C_6H_5CHBrCH_3$, is beclouded by the fact that at least three investigators[3,7,12] could not repeat the reaction even with racemic starting material, and that the active bromide, if obtained, should have racemized extensively under the conditions of the reaction.[6,13] In the other instance,[7] the activity of the product was so slight that a small amount of asymmetric induction may be responsible for it.

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