

Decomposition of Alkyl Hypochlorites. The 4-*t*-Butylcyclohexyl Radical<sup>1</sup>

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4-*t*-Butylcyclohexyl radical, generated from dimethyl(*cis*- and *trans*-4-*t*-butylcyclohexyl)carbonyl hypochlorite and from *cis*- and *trans*-4-*t*-butylcyclohexanecarbonyl peroxide, reacts with halogen donors (carbon tetrachloride, bromotrichloromethane, alkyl hypochlorite) to yield *cis*- and *trans*-4-*t*-butylcyclohexyl halide (chloride and bromide) in which *cis* halide predominates over *trans* halide by 2:1. Stereospecificity (*cis*-*trans*) decreases slightly with decreasing temperature. The results are compared with data on norbornyl systems.

Tertiary alkyl hypochlorites have been shown in a number of cases to undergo decomposition to alkyl halides and carbonyl compounds.<sup>2,3</sup> The sensitivity of decomposition to light, radical sources, and inhibitors points to decomposition by a free-radical chain route. In this report attention is called to the use of hypochlorites for the study of radicals, illustrated here by an investigation of the 4-*t*-butylcyclohexyl radical.

## Results

Decomposition of dimethyl(*cis*- or *trans*-4-*t*-butylcyclohexyl)carbonyl hypochlorite in an inert medium by weak irradiation or by heat affords in high yield a mixture of *cis*- and *trans*-4-*t*-butylcyclohexyl chlorides in the ratio of 2:1. Exactly the same ratio of chlorides is obtained from either *cis* or *trans* starting material at all temperatures measured. In control experiments pure *cis* and pure *trans* chloride were observed to be stable to the decomposition conditions and to the conditions of analysis. The data are summarized in Table I.

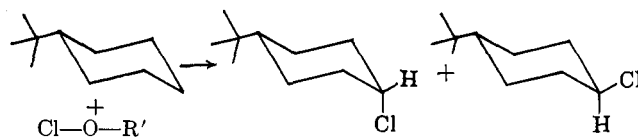
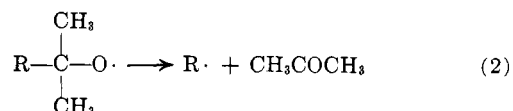
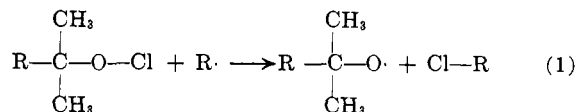
Assignment of structure to the chlorides is based on the identity with samples prepared from 4-*t*-butylcyclohexanol. Assignment of *cis* stereochemistry to the chloride of shorter retention time on a nitrile silicone column is based on (1) its enhanced ease (in comparison with *trans* isomer) of conversion by base to 4-*t*-butylcyclohexene<sup>4</sup>; (2) location in the n.m.r. spectrum of the C-1 hydrogen at  $\tau$  5.63 (*vs.*  $\tau$  6.36 for the *trans* isomer)<sup>5</sup>; (3) location in the infrared spectrum of the C-Cl stretching band at 690  $\text{cm}^{-1}$  (*vs.* 725  $\text{cm}^{-1}$  for the *trans* isomer),<sup>6</sup> and a marked similarity in infrared spectra of the *cis* and *trans* chlorides with the corresponding *cis* and *trans* bromides of known configuration.<sup>7</sup>

Decomposition of the diacyl peroxide of *trans*-4-*t*-butylcyclohexanecarboxylic acid has been effected under three sets of conditions: (1) in carbon tetrachloride, (2) in bromotrichloromethane,<sup>8</sup> and (3) in carbon tetrachloride containing bromine. The data

are summarized in Table II. Analysis was made for the 4-*t*-butylcyclohexyl chlorides and bromides.<sup>9</sup> In this case also *cis*-4-*t*-butylcyclohexyl chloride is favored over the *trans* isomer, with a slightly larger preference than noted with the hypochlorites. From the decomposition in bromotrichloromethane, *cis* bromide predominates over *trans* bromide by 2:1. Decomposition in carbon tetrachloride containing bromine affords both the chlorides and the bromides. The chlorides are formed in essentially the same ratio as in the absence of bromine. The apparent preference for *trans* bromide is complicated by the instability of the *cis* bromide. In control experiments it was shown that both bromides are somewhat unstable under these experimental conditions and that the *cis* bromide is the less stable of the two (47% destruction of the *cis* isomer under conditions resulting in only 13% destruction of the *trans* isomer).

## Discussion

The stability of the hypochlorites in the dark and their sensitivity to light, to initiators, and to inhibitors indicate decomposition by a free-radical chain reaction, in accord with previous data on tertiary hypochlorites.<sup>2,3</sup> The identity of the ratio of *cis*- to *trans*-4-*t*-butylcyclohexyl chloride starting from either *cis* or *trans* hypochlorite is in accord with this view and implicates the 4-*t*-butylcyclohexyl radical as a common intermediate for the two cases. An unexpected feature is the preferential formation of the *cis* (axial) chloride over the *trans* (equatorial) chloride, a pattern that is also found in the decomposition of the *cis*- and *trans*-4-*t*-butylcyclohexanecarbonyl peroxides (Table II). [Although we have not effected the equilibration of these chlorides, control data (see Ex-



(9) As reported previously [H. H. Lau and H. Hart, *J. Am. Chem. Soc.*, **81**, 4897 (1959)], these are the minor products of decomposition. The major products appear to be more complicated than originally reported and are under reinvestigation.

(1) Supported in part by the National Science Foundation and by the Atomic Energy Commission under Contract No. AT(30-1)-905. A preliminary report of this work appeared in *J. Am. Chem. Soc.*, **84**, 2463 (1962).

(2) F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

(3) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593, 1597 (1963).

(4) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

(5) (a) A. J. Berlin and F. R. Jensen, *Chem. Ind. (London)*, 995 (1960);

(b) L. W. Reeves and K. O. Strømme, *Can. J. Chem.*, **38**, 1241 (1960).

(6) E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 217.

(7) E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **24**, 143 (1959). We wish to thank Professor Eliel for infrared spectra of the *cis* and *trans* bromides.

(8) Attempts were also made to decompose the hypochlorite in bromotrichloromethane. Although the peroxide gave reproducible results in this solvent, the hypochlorite results were variable and consequently have not been included in this report.

TABLE I  
PRODUCTS FROM THE DECOMPOSITION<sup>a</sup> OF DIMETHYL(*cis*- AND *trans*-4-*t*-BUTYLCYCLOHEXYL)CARBINYL HYPOCHLORITE

Solvent	Concn., <i>M</i>	Temp., °C.	Ratio of RCl <sup>b,c</sup>		Yield of RCl, %
			<i>cis</i>	<i>trans</i>	
<i>trans</i> Hypochlorite					
CCl <sub>4</sub>	0.37	80	67	33	93
CCl <sub>4</sub>	0.40	0	65	35	84
CCl <sub>4</sub>	0.37	-30	62	38	68
CFCl <sub>3</sub>	0.34	0	65	35	99
CFCl <sub>3</sub>	0.34	-80	58	42	83
CCl <sub>4</sub> <sup>d</sup>	0.38	80 <sup>d</sup>	66	34	49
<i>cis</i> Hypochlorite					
CCl <sub>4</sub>	0.4	80	67	33	85
CCl <sub>4</sub>	0.4	0	65	35	80
CCl <sub>4</sub>	0.4	-30	62	38	79
CFCl <sub>3</sub>	0.28	0	66	34	
CFCl <sub>3</sub>	0.32	-80	58	42	94
Cyclohexane	0.06	10	67	33	84

<sup>a</sup> Weak irradiation, ref. 21. <sup>b</sup> RCl is 4-*t*-butylcyclohexyl chloride. <sup>c</sup> Precision of ratios,  $\pm 0.5\%$ . <sup>d</sup> Thermal decomposition.

TABLE II  
PRODUCTS FROM THE THERMAL DECOMPOSITION OF BIS-*trans*-4-*t*-BUTYLCYCLOHEXANECARBONYL PEROXIDE

Solvent	Concn., <i>M</i>	Temp., °C.	Ratio of RCl <sup>a</sup>		Yield, %	Ratio of RBr <sup>a</sup>		Yield, %
			<i>cis</i>	<i>trans</i>		<i>cis</i>	<i>trans</i>	
CCl <sub>4</sub>	0.05	90	73	27	30			
CCl <sub>4</sub> <sup>b</sup>	0.18	90	73	27				
CCl <sub>4</sub>	0.1	80	73	27	20			
CBrCl <sub>3</sub> <sup>c</sup>	0.1	80				69	31	
CCl <sub>4</sub> <sup>c,d</sup>	0.1	80				37 <sup>e</sup>	63	6
CCl <sub>4</sub> <sup>f</sup>	0.01	80	(69) <sup>g</sup>	(31) <sup>g</sup>	0.8	40 <sup>e</sup>	60	12
CCl <sub>4</sub> <sup>h</sup>	0.001	80	(77) <sup>g</sup>	(23) <sup>g</sup>	9	43	57	14

<sup>a</sup> R is 4-*t*-butylcyclohexyl. <sup>b</sup> In this run bis-*cis*-4-*t*-butylcyclohexanecarbonyl peroxide was used. <sup>c</sup> Carried out in amber vessels. <sup>d</sup> Contains bromine, 0.2 *M*. <sup>e</sup> Preferential destruction of *cis* isomer; see description of control data. <sup>f</sup> Contains bromine, 0.02 *M*. <sup>g</sup> Owing to the small yield of RCl, these figures are not so accurate as others. <sup>h</sup> Contains bromine, 0.002 *M*.

TABLE III  
EFFECT OF ATOM-TRANSFER AGENT ON *cis*- TO *trans*-4-*t*-BUTYLCYCLOHEXYL HALIDE RATIO FROM 4-*t*-BUTYLCYCLOHEXYL RADICAL AT 80°

Reactant	Solvent	Transfer agent	<i>cis-trans</i> R-X	
			<i>cis</i>	<i>trans</i>
Hypochlorite	CCl <sub>4</sub>	RO-Cl	2:1	
Peroxide	CCl <sub>4</sub>	Cl <sub>3</sub> C-Cl	2.7:1	
Peroxide	CCl <sub>3</sub> Br	Cl <sub>3</sub> C-Br	2.2:1	
Peroxide	CCl <sub>4</sub>	Br-Br	(~1:1) <sup>a</sup>	

<sup>a</sup> Values uncertain owing to instability of products under reaction conditions (see Table II).

perimental section, Table IV) and data from other systems indicate that chlorine in the axial position is less stable than in the equatorial position.<sup>5b,10]</sup> The slightly different *cis-trans* product ratio from hypochlorite *vs.* peroxide is probably associated with different halogen donors in the two cases. That the 4-*t*-butylcyclohexyl radical is sufficiently selective to search out good halogen donors is clear from the last three entries of Table II, from which one may estimate that the  $\Delta F^*$  of the step in which alkyl chloride is formed exceeds by more than 6.5 kcal. the  $\Delta F^*$  of the alkyl bromide-forming step.

In Table III are summarized the observations bearing on the effect of atom-transfer reagent on the stereospecificity of 4-*t*-butylcyclohexyl radical. Thus *cis* halide is favored over *trans* halide for all of these halogen donors except molecular bromine; for this case, the selectivity appears to be lower but interpretation is obscured by the instability of the products to the reaction conditions.

(10) Ref. 6, p. 236.

**Norbornyl Radicals.**—A related case in which the stereochemistry of halogen atom transfer to a secondary radical has been examined is the halogenation of norbornane.<sup>11</sup> One notes that the preferential forma-



Conditions	Transfer agent	Yield, %	
		<i>exo</i>	<i>endo</i>
$h\nu$	Cl-Cl	73	22
(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub>	Cl <sub>3</sub> C-Cl	95	1-5

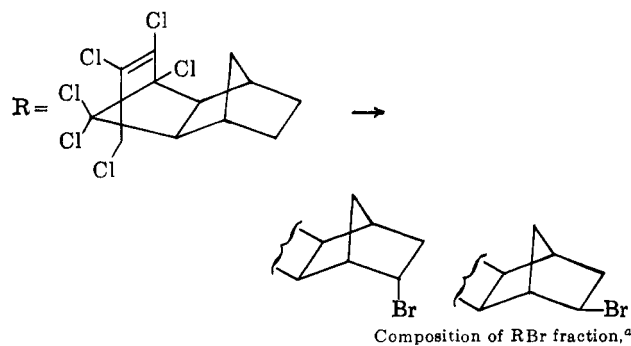
tion of one isomer (*exo*) over the other (*endo*) is considerably greater than in the case of the 4-*t*-butylcyclohexyl system.

Similar selectivity is also observed with the dihydroaldrinyl radical (R).<sup>12</sup>

**Hunsdiecker Reactions.**—Investigations of the Hunsdiecker reaction and the Cristol-Hunsdiecker reaction (RCOOH-HgO-X<sub>2</sub>)<sup>12b</sup> on 2-*exo*-dihydroaldrincarboxylic acid led to an *exo-endo* bromide ratio of 70:30, comparable to the low selectivity in the reaction of bromine with the dihydroaldrinyl radical. In a study of the Hunsdiecker reaction with 4-*t*-butylcyclohexanecarboxylic acid,<sup>7</sup> a *trans-cis* bromide ratio of 65:35 was reported (total yield of bromides, ~25%). In a

(11) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

(12) (a) S. J. Cristol, J. R. Douglass, W. C. Firth, Jr., and R. E. Krall, *J. Org. Chem.*, **27**, 2711 (1962); (b) S. J. Cristol, L. K. Gaston, and T. Tiedeman, *ibid.*, **29**, 1279 (1964).



Radical source	Transfer agent	<i>endo</i>	<i>exo</i>
<i>exo</i> -(R-COO) <sub>2</sub>	Br-Br	30	70
<i>exo</i> -(RCOO) <sub>2</sub>	Cl <sub>3</sub> C-Br	0	100
<i>endo</i> -(RCOO) <sub>2</sub>	Cl <sub>3</sub> C-Br	0	100

<sup>a</sup> Product analysis by infrared method. Results reported as accurate to  $\pm 4\%$ .

repetition of this experiment, we also observed a predominance of *trans* bromide, but, in view of the low yields and the finding of selective destruction of the *cis* bromide under the conditions of the experiment, further reinvestigation of this Hunsdiecker reaction was discontinued.

#### Effect of Temperature on *cis-trans* Chloride Ratio.—

The long chain nature of the decomposition of the hypochlorites of Table I permitted the evaluation of the *cis-trans* chloride ratio over a wide temperature range. Although the change is small, it is reproducible and is the same for both reactants. A surprising feature is the *decrease* in selectivity as the temperature is lowered.

$$\begin{aligned} \Delta H_{cis}^* - \Delta H_{trans}^* &= 0.3 \text{ kcal./mole} \\ \Delta S_{cis}^* - \Delta S_{trans}^* &= +2 \text{ e.u.} \end{aligned}$$

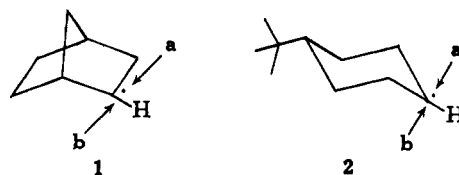
Thus the preferential formation of *cis*- over *trans*-4-*t*-butylcyclohexyl chloride in halogen atom abstraction by the 4-*t*-butylcyclohexyl radical is due to a more favorable entropy of activation.

**4-*t*-Butylcyclohexyl Radical.**—The major feature requiring interpretation in this work is the preference for transfer of an atom to the 4-*t*-butylcyclohexyl radical to form an axial-bonded substituent, compared with the large preference to form an equatorial (*exo*) substituent in transfer to the norbornyl radicals.<sup>11,12</sup> At one point, consideration was given to explanation in terms of radicals pyramidal rather than planar at the carbon holding the odd electron.<sup>13</sup> However, recent evidence from electron paramagnetic resonance (e.p.r.) points strongly to the planar form as the stable geometric array for carbon radicals.<sup>14</sup> (Out of sixteen radicals, acyclic and cyclic including cyclohexyl, that might be expected to have the odd electron in a p-orbital, only cyclopropyl radical showed an  $\alpha$  constant [ $a_{\alpha-H}$ ] outside the range of 21–23 gauss.<sup>13</sup>) The e.p.r. data on cyclohexyl radical also indicate nonequivalence of the  $\beta$ -hydrogens,  $a_{\beta\text{-axial H}} = 41$  gauss ( $a_{\beta\text{-equatorial H}} = 5$  gauss).<sup>15</sup> The substantial preference for approach from direction **a** over **b** in the 2-norbornyl radical, plus the *decrease* in selectivity with decreasing

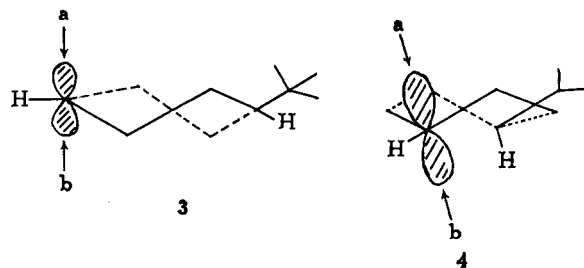
(13) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(14) The strongest evidence for planarity of a radical would appear to lie in the carbon-13 hyperfine interaction constant, to date reported only for methyl radical [M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961)].

(15) Detailed consideration of e.p.r. data on the cyclohexyl radical will appear in a forthcoming publication by R. W. Fessenden and R. H. Schuler.



temperature in this work make it seem likely that the geometry of the 4-*t*-butylcyclohexyl moiety at the transition state for the atom-transfer step which produces *cis* chloride may be appreciably removed from a chair conformation<sup>16</sup> (a point of relevance to other questions of stereochemistry of radical additions to olefins).<sup>17</sup> Two different twist-boat conformations are represented in **3** and **4**. In **3**, atom transfer from directions **a** and **b** appear equally favorable; in **4**, transfer from direction **a** (leading to *cis* product) appears more favorable than transfer from direction **b**. However, the preference for *cis* over *trans* product is energetically a small value ( $\Delta F_{trans}^* - \Delta F_{cis}^* = 0.4$  kcal./mole) and the above consideration is no more than suggestive. It is of interest that 1-hydroxycyclohexyl radicals react with 1-octene to afford product mixtures in which equatorial product predominates.<sup>18a</sup> Also related to this problem are the results of halogenation of 1-chloro- and 1-bromocyclohexane. The ratio of *cis* to *trans* in the 1,4-dihalocyclohexane fraction is less than one when the halogen donor is chlorine and greater than one when the donor is *t*-butyl hypochlorite.<sup>18b</sup>



## Experimental

All melting points are corrected; boiling points are uncorrected.

***cis*- and *trans*-4-*t*-Butylcyclohexanecarboxylic Acid.**—The *cis* isomer was obtained by the procedure of Lau and Hart, m.p. 116–118° (lit.<sup>9</sup> m.p. 117–118°), and the *trans* isomer, by the procedure of Tichý, Jonáš, and Sicher, m.p. 174.5–175° (lit.<sup>19</sup> m.p. 174–175°).

**Dimethyl(*cis*- and *trans*-4-*t*-butylcyclohexyl)carbinols** were prepared from the corresponding methyl esters by the action of methyl Grignard reagent: *cis* isomer, m.p. 49–50° after recrystallization from acetonitrile (lit.<sup>20</sup> m.p. 49.5–50°); *trans* isomer, m.p. 101.5–102° after recrystallization from acetonitrile (lit.<sup>20</sup> m.p. 103–104°).

(16) An alternate explanation has recently been advanced by M. C. R. Symons [*Nature*, **198**, 1196 (1963)]; preferential attack from **b** in **2** is attributed to "electron-rich chlorine" avoiding the region of higher electron density (region **a** was considered of higher electron density based on the greater interaction constant of the radical with the  $\beta$ -axial hydrogens). The suggestion is an interesting one, but we feel that the halogen of hypochlorite or of carbon tetrachloride will be more negative at the transition state than at the ground state and would prefer reaction at sites of higher electron density.

(17) For a review of "Stereochemistry of Free Radical Additions to Olefins," see B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962); see also D. G. Applequist and N. D. Werner, *J. Org. Chem.*, **28**, 48 (1963).

(18) (a) R. J. Gritter and R. L. Albers, *ibid.*, **27**, 4708 (1962); (b) G. A. Russell, A. Ito, and R. Konaka, *J. Am. Chem. Soc.*, **85**, 2988 (1963).

(19) M. Tichý, J. Jonáš, and J. Sicher, *Collection Czech. Chem. Commun.*, **24**, 3434 (1959).

(20) R. D. Stolow and C. B. Boyce, *J. Org. Chem.*, **26**, 4726 (1961).

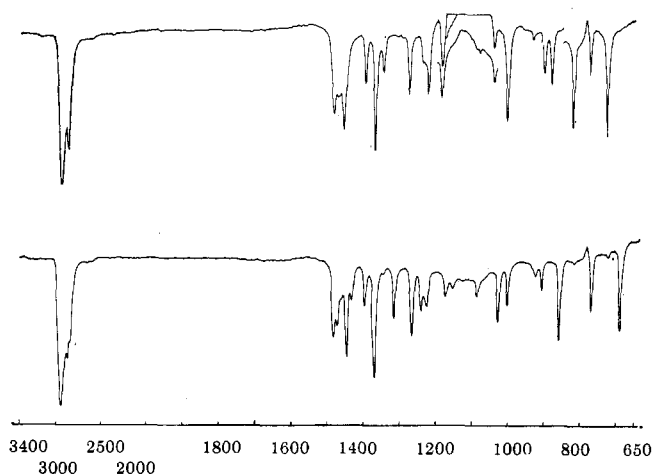


Fig. 1.—4-*t*-Butylcyclohexyl chloride: *trans* isomer (upper curve), *cis* isomer (lower curve). Both spectra were measured in carbon tetrachloride from 3400–900  $\text{cm}^{-1}$  and in carbon disulfide from 900–650  $\text{cm}^{-1}$ .

Dimethyl(*cis*- and *trans*-4-*t*-butylcyclohexyl)carbonyl hypochlorites were prepared from the corresponding alcohols by the method described previously<sup>2</sup> in yields of 80–95%.

**Decomposition of Hypochlorites (see Table I).**—A 0.4 *M* solution of the hypochlorite in the desired solvent, protected from the light by wrapping with aluminum foil, was swept with prepurified nitrogen for 1 hr. at 0° and then irradiated with a weak ultraviolet source<sup>21</sup> for 10 min. The color of the hypochlorite disappeared in 5 min. For decompositions at –30 and +80°, aliquots of hypochlorite solution in test tubes containing glass-enclosed magnet bars, protected from light, were degassed and sealed. The foil-wrapped tubes were placed in a bath at the required temperature for 2-min. warm-up time; the foil was removed and the solution was irradiated<sup>21</sup> with stirring until disappearance of the yellow color. Analysis of products was made by gas-liquid phase chromatography (g.l.p.c.) using XF-1150 (General Electric nitrile silicone fluid) on Chromosorb P or TCEP (1,2,3-tri- $\beta$ -cyanoethoxypropane). In all runs except those employing Freon 11 (trichlorofluoromethane), the solution from the decomposition was analyzed directly. Quantitative analysis was made by use of cyclohexanone as internal standard by the procedure outlined previously.<sup>2</sup> When Freon 11 was used as solvent, it was evaporated through a Vigreux column, or carbon tetrachloride was added to make a final volume of 2.0 or 5.0 ml. before analysis.

**Identification of Products.**—In a typical run, a 0.4 *M* solution of hypochlorite in carbon tetrachloride was decomposed at 0°. Analysis of an aliquot on a 20% TCEP column (0.6  $\times$  200 cm.) at 91°, helium pressure 15 p.s.i., showed five peaks: 0.6 min. (carbon tetrachloride), 1.3 min. (acetone), 12.7 and 14.7 min. (*cis*- and *trans*-4-*t*-butylcyclohexyl chlorides), and 26.5 min. (a minor peak, unidentified). Separation of chlorides was improved by use of a 15% XF-1150 column (0.9  $\times$  200 cm.) at 94°, 15 p.s.i., which showed peaks at 59 min. (*cis* chloride) and 69 min. (*trans* chloride). The compound of 59-min. retention time, *cis*-4-*t*-butylcyclohexyl chloride, was collected and redistilled at 0.3 mm. and 80° (bath temp.).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{18}\text{Cl}$ : C, 68.74; H, 10.96; Cl, 20.30. Found: C, 68.91; H, 10.97; Cl, 20.40.

The infrared spectrum is given in Fig. 1.

A solution of 2.1 g. of a *cis*-*trans* mixture of chlorides from a decomposition, and 2 g. of potassium hydroxide in 10 ml. of 95% ethanol was heated at reflux for 19 hr. The mixture was poured into water and extracted with petroleum ether (b.p. 30–60°). Washing, drying, and removal of the solvent afforded 1.5 g. of oil; g.l.p.c. analysis showed a peak at 9 min. (4-*t*-butylcyclohexene) and at 69 min. (*trans*-4-*t*-butylcyclohexyl chloride). The latter was collected and redistilled.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{18}\text{Cl}$ : C, 68.74; H, 10.96; Cl, 20.30. Found: C, 68.62; H, 10.88; Cl, 20.28.

The infrared spectrum is given in Fig. 1.

***cis*- and *trans*-4-*t*-Butylcyclohexyl Chloride.**—To a mixture of 15.6 g. (0.1 mole) of 4-*t*-butylcyclohexanol (a 1:4 *cis*-*trans* mixture) and 18.5 g. (0.1 mole) of tri-*n*-butylamine in 150 ml. of anhydrous ether at 25° was added with stirring 12 g. (0.1 mole) of thionyl chloride in 50 ml. of anhydrous ether over a period of 1 hr. The mixture was stirred at 25° for 3 hr. and poured onto ice-water; the ether layer was washed with water, dried over magnesium sulfate, and filtered; the ether was removed. Distillation afforded a 7.4-g. fraction (b.p. 48–60° at 10 mm.). Redistillation through a 30-cm. spinning platinum band column gave a 3.3-g. fraction (b.p. 60–65° at 12 mm.) of 4-*t*-butylcyclohexene, a 2.9-g. fraction (b.p. 80–85° at 12 mm.) of the isomeric chlorides (largely *cis*), and unchanged alcohol. The chloride fraction, analyzed by g.l.p.c. on an XF-1150 column at 97°, showed peaks at 8.7 (4-*t*-butylcyclohexene), 57.5, and 64.5 min. The 57.5-min. peak was collected; the infrared spectrum was identical with the spectrum of the sample assigned the structure of *cis* chloride obtained from the decomposition of the hypochlorites.

A 2.0-g. sample of a *cis*-*trans* mixture of the chloride was treated with ethanolic potassium hydroxide, as described above, to destroy the *cis* isomer. The product no longer showed the 57.5-min. peak; the 64.5-min. peak was collected; its infrared spectrum was identical with that of the compound described as *trans*-4-*t*-butylcyclohexyl chloride isolated from the decomposition of the hypochlorites.

***cis*- and *trans*-4-*t*-butylcyclohexyl bromides** were prepared by a published procedure.<sup>7</sup> The separation was effected on an XF-1150 column at 122° and the retention time of *cis* bromide was 45 min., *trans* bromide, 48 min. A sample of pure *cis* bromide was obtained by collection from the column; obtention of pure *trans* was effected by destruction of *cis* isomer by base (see above) followed by g.l.p.c. collection. The infrared spectra of the *cis* and *trans* bromides were identical with those of authentic samples.<sup>7</sup>

**4-*t*-Butylcyclohexanecarbonyl Chloride.**—A mixture of *trans*- or *cis*-4-*t*-butylcyclohexanecarboxylic acid and an excess of thionyl chloride was allowed to stand at room temperature for 3–4 hr., and the excess thionyl chloride was removed under reduced pressure at ~40–50°. The thionyl chloride used was a commercial product (Eastman Kodak White Label) distilled over linseed oil<sup>22</sup> immediately before use. When the reaction mixture was heated at a higher temperature or unpurified thionyl chloride was used, epimerization took place to an extent of 15%. This was analyzed by g.l.p.c. by converting the acid chlorides to the methyl ester with methanol using the methyl esters prepared from the corresponding acids with diazomethane for reference. Retention times were 19 min. for the *trans* ester and 30 min. for the *cis* ester (TCEP column at 114° and 15 p.s.i.).

***trans*-4-*t*-Butylcyclohexanecarbonyl Peroxide.**—Since some difficulty was experienced in preparation by the published procedure,<sup>9</sup> the following modification is described in detail. To a stirred solution of 3.15 g. (89% purity, *i.e.*, 0.036 mole) of sodium peroxide in 80 ml. of ice-water was added 9.7 g. of 4-*t*-butylcyclohexanecarbonyl chloride (85% *trans* isomer) in 50 ml. of *n*-hexane over a period of 20 min. at –2 to 0°. After stirring at 0° for an additional 2.5 hr., 50 ml. of ether was added to the reaction mixture; the organic layer was washed and dried over calcium chloride at 0°. Filtration and removal of solvent under reduced pressure afforded 5.7 g. of white crystals, m.p. 87–89°, 66% yield. Recrystallization from *n*-hexane gave crystals melting at 88–89°, lit.<sup>9</sup> m.p. 89°. Iodometric analysis gave variable results. The best criteria of purity were the melting point and the infrared spectrum: the characteristic double peak at 1775 and 1800  $\text{cm}^{-1}$  and no other bands in carbonyl absorption region.

***cis*-4-*t*-Butylcyclohexanecarbonyl peroxide** was prepared from the pure *cis* acid chloride by the above procedure, using a temperature of –10 to –5° in 40 and 90% purity, estimated yield from infrared spectrum at 1780 and 1800  $\text{cm}^{-1}$ .

**Decomposition of *cis*- and *trans*-4-*t*-Butylcyclohexanecarbonyl Peroxide (see Table II).**—A sample of the peroxide in the desired solvents was degassed by a nitrogen stream, sealed, and heated at the desired temperature for 15–20 hr. In the runs with bromine, the bromine was added immediately after the degassing step. Dark brown flasks were used for the bromine and the bromotrichloromethane experiments.

(21) Burton Ultraviolet Black Lamp, Model 1910 (a weak ultraviolet source), Burton Manufacturing Co., Santa Monica, Calif.

(22) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 381.

In one run, 563 mg. (1.5 mmoles) of the *trans* peroxide was decomposed in 15 ml. of carbon tetrachloride. Solvent was removed through a Vigreux column and the residue was chromatographed on 12 g. of activity grade IV alumina (the chlorides were shown to be stable to the isolation procedure), eluting with a 1:2 benzene-petroleum ether mixture. The first 15 ml. afforded 345 mg. of oil. Analysis on an XF-1150 column at 106° showed peaks at 16 min. (hexachloroethane), 38 min., and 43 min. Samples of the latter two peaks were collected; the infrared spectra were identical with those of *cis*- and *trans*-4-*t*-butylcyclohexyl chloride, respectively.

A 738-mg. sample (2 mmoles) of *trans* peroxide was decomposed in 20 ml. of bromotrichloromethane. The alkyl halide fraction was isolated as described above. Analysis on an XF-1150 column indicated hexachloroethane and *cis*- and *trans*-4-*t*-butylcyclohexyl bromide. The chloride peaks were not present. The bromides were collected by use of a preparative g.l.p.c. column; the infrared spectra were identical with those of authentic samples.

In the peroxide decompositions in carbon tetrachloride with bromine added, the isomeric chlorides and bromides were identified by comparison of retention times.

**Control Experiments. A. Stability of *cis*-4-*t*-Butylcyclohexyl Chloride to Hypochlorite Decomposition Conditions.**—To a 1.2 *M* solution of diethylisopropylcarbinyl hypochlorite in carbon tetrachloride was added an equal volume of a 0.12 *M* solution of the *cis* chloride in carbon tetrachloride. The solution was swept with nitrogen for 1 hr. and then decomposed by weak ultraviolet light at 0°. Product analysis by g.l.p.c. showed isopropyl chloride, diethyl ketone, diethylisopropylcarbinol, and *cis*-4-*t*-butylcyclohexyl chloride. Quantitative analysis by use of internal standard added after completion of reaction indicated that the amount of the *cis* chloride was unchanged.

**B. Behavior of 4-*t*-Butylcyclohexyl Bromides to Peroxide Decomposition Conditions.**—In order to test the suitability of cyclohexanecarbonyl peroxide in this control equipment, the peroxide was first decomposed in the absence of added bromide. A solution of 940 mg. of cyclohexanecarbonyl peroxide (purity, 70% by iodometric analysis, 650 mg., 2.5 mmoles) and 1 g. (0.32 ml., 6 mmoles) of bromine in 10 ml. of carbon tetrachloride was heated at 70° for 16 hr. in a brown flask. After cooling, it was washed with sodium thiosulfate solution, 5% sodium bicarbonate solution, and water and dried over magnesium sulfate; the solvent was removed giving 944 mg. of brown oil. Analysis by g.l.p.c. using a TCEP column at 121° had peaks at 5 min. (cyclohexyl bromide), 16 min., and 28 min. (both unidentified). A sample of the *cis*- and *trans*-4-*t*-butylcyclohexyl bromides was added to the product mixture. The retention times for these bromides were 21 and 24 min., respectively, with no interference from either the 16- or the 28-min. peaks.

In another experiment, a 66.2-mg. sample of *cis*-4-*t*-butylcyclohexyl bromide and a 65.9-mg. sample of the *trans* bromide were dissolved in 5 ml. of carbon tetrachloride. To a 4-ml. portion of this solution was added 300 mg. (70% purity, 210 mg., 0.85 mmole) of cyclohexanecarbonyl peroxide and 310 mg. of bromine; carbon tetrachloride was added to a total volume of 100 ml. The solution was heated at 75° for 16 hr. in an

TABLE IV  
CONTROL EXPERIMENTS ON *cis*- AND *trans*-4-*t*-BUTYLCYCLOHEXYL HALIDES

Reactants	Conditions	Results
<i>cis</i> -Br	BrCCl <sub>3</sub> , 25°, dark	No change (4.5 days)
<i>cis</i> -Br	BrCCl <sub>3</sub> , 25°, daylight	After 1 day, no <i>cis</i> -Br, 33% conversion to <i>trans</i> -Br
<i>cis</i> -Cl (0.71) and <i>trans</i> -Cl (0.29)	BrCCl <sub>3</sub> , 25°, dark	No change (6 days)
<i>cis</i> -Cl (0.71) and <i>trans</i> -Cl (0.29)	BrCCl <sub>3</sub> , 25°, daylight	30% disappearance of <i>cis</i> , 25% increase in <i>trans</i> after 3 days; 75% disappearance of <i>cis</i> , 50% increase in <i>trans</i> after 6 days
<i>trans</i> -Cl	BrCCl <sub>3</sub> , 25°, daylight	No change (15 days)
<i>cis</i> -Cl	BrCCl <sub>3</sub> , 25°, daylight	After 3 days, 30% <i>cis</i> , 70% <i>trans</i> (positive identification by collection from v.p.c.)
<i>cis</i> -Cl	BrCCl <sub>3</sub> , 25°, daylight 2,6-Di- <i>t</i> -butyl-4-methylphenol	No change (6 days)
<i>cis</i> -Cl	CCl <sub>4</sub> , Br <sub>2</sub> , 25°, dark	No change (5 days)
<i>cis</i> -Cl	CCl <sub>4</sub> , Br <sub>2</sub> , 25°, daylight	After 3.5 days, 60% <i>cis</i> , 40% <i>trans</i>
<i>cis</i> -Cl	CCl <sub>4</sub> , HBr, 25°, daylight	No change (5 days)

amber flask, cooled, washed with sodium thiosulfate solution, 5% sodium bicarbonate solution, and water, and dried over magnesium sulfate. After removal of the solvent under reduced pressure through a Vigreux column, the residual oil was analyzed on an XF-1150 column (*cis* bromide: initial, 53 mg.; final, 28.2 mg.; destruction, 47%; *trans* bromide: initial, 52.7 mg.; final, 45.8 mg.; destruction, 13%).

**C. Behavior of *cis*- and *trans*-4-*t*-Butylcyclohexyl Halides towards Light, Bromine, and Other Conditions.**—The data are summarized in Table IV. Product analyses were made by the procedures described above.

**D. Behavior of the Alkyl Halides on Alumina Chromatography.**—Chromatography of a 2:1 *cis*-*trans* mixture of 4-*t*-butylcyclohexyl chlorides on activity grade III alumina afforded quantitative recovery; g.l.p.c. analysis showed that the *cis*-*trans* ratio was unchanged.

Chromatography of a sample of *cis*-4-*t*-butylcyclohexyl bromide on activity grade IV alumina afforded 92% recovery. G.l.p.c. analysis showed a small peak corresponding to 4-*t*-butylcyclohexene, a large peak at *cis* bromide, and the absence of the *trans* bromide peak, *i.e.*, a small amount of dehydrobromination of the *cis* bromide but no isomerization to the *trans* isomer.