tion mechanism proposed for the isomerization of the xylenes using a zeolite catalyst may also be operative in an acid-catalyzed system but obscured by hydrocarbon–catalyst complex formation.

Experimental Section

The di- and trimethylbenzenes were obtained from Matheson Coleman and Bell, Norwood, Ohio, and were used without further purification. The xylenes were all over 99.8% pure and the trimethylbenzenes were all over 96.7% pure. The crystalline catalyst was synthesized from Type Y zeolite with a SiO_2/Al_2O_3 molar ratio of 5.0 by partial rare earth cation exchange (45% rare earth) and partial decationization (50%). The balance of the cations was sodium. The preparation and pertinent properties of this material have been previously reported.[5,6]

The batch experiments were carried out in a 250-ml Hartalloy Magnadash, a magnetically stirred autoclave fitted with a dip-tube for withdrawing samples. Five grams of catalyst powder was used for 0.5 mol of xylene.

The flow experiments were carried out in a high-pressure stainless steel fixed bed reactor of conventional design. For these experiments the catalyst was used in the form of $^1/_8$ in. × $^1/_8$ in. tablets. The reaction temperature and pressure were maintained at 300° and 500 psig respectively in all experiments. The hydrogen to hydrocarbon ratio was held at 5:1 while the space velocities varied between 0.5 and 20 g of feed/g of catalyst/hr.

The analyses were made on a Perkin-Elmer 880 chromatograph equipped with 150-ft [*m*-bis(*m*-phenoxyphenoxy)benzene–Apiezon L] capillary column and a flame ionization detector.

Registry No.—*o*-Xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; 1,2,3-trimethylbenzene, 526-73-8; 1,3,5-trimethylbenzene, 108-67-8; 1,2,4-trimethylbenzene, 95-63-6.

The Stereochemistry of Free-Radical Additions of Thiols to Substituted Cyclohexenes[1]

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Radical chain addition of hydrogen bromide to 2-chloro-4-*t*-butylcyclohexene (**1**) gave exclusively 2^c-chloro-4^c-*t*-butylcyclohexyl bromide (**8**), the product of *trans*-diaxial addition. AIBN- and uv-initiated free-radical additions of benzyl mercaptan (A), hydrogen sulfide (B), methanethiol (C), and thiolacetic acid (D) to 1- and 2-chloro- and 1- and 2-methyl-4-*t*-butylcyclohexene (**3**, **1**, **4**, and **5**, respectively) were investigated. The relative proportions of the diastereomeric adducts produced under varying reaction conditions were determined for the following reactions: A and **1**; B and **3** and **1**; C and **3** and **1**; D and **1** and **3**–**5**. In all cases, *trans*-diaxial addition predominated, and the relative proportions of products were shown to be dependent upon the addendum to olefin ratio. Conformational energy factors associated with the transition state appear to be responsible for preferential axial attack by a thiyl radical. The lower stereoselectivity of thiol additions, as contrasted to those of hydrogen bromide, are best explained in terms of a reversal of the thiyl-radical addition step. Differences in the extent of this reversibility appear to be dependent upon the relative stabilities of the thiyl radicals and the 2-thiyl-1-substituted cyclohexyl radicals, as well as on the rate of chain transfer. Bridged thiyl radical intermediates are not considered important in these additions. The concentration and temperature effects observed for free-radical additions of thiols to 1- and 2-chloro-4-*t*-butylcyclohexene compared with those observed for additions to 1- and 2-methyl-4-*t*-butylcyclohexene are of the same order of magnitude, but in opposite directions. The energy difference between the cyclohexyl-radical intermediates arising from "equatorial" thiyl-radical attack is probably responsible for the opposing trends. The extent of reversibility of the initial radical addition step is greatest for hydrogen sulfide and thiolacetic acid, less for methanethiol, and nonexistent for hydrogen bromide.

Free-radical additions of hydrogen bromide to various 1-substituted cyclohexenes have been reported to proceed exclusively in a *trans*, anti-Markovnikov manner.[2,3] On the other hand, the addition of thiol compounds was shown to be nonstereospecific;[4,5] a mixture of isomers was obtained in which the *trans*-addition product predominated. Several explanations have been offered to account for these results.[4-6] One of the factors taken into consideration was a chair–chair interconversion of the intermediate radical formed in the addition step. The importance of such chair–chair interconversions in the nonstereospecific additions of thiols can presumably be ascertained by causing the six-membered ring to prefer a single conformation.[7] To this end, we have chosen to study the stereochemistry of the radical-chain additions of hydrogen bromide to 2-chloro-4-*t*-butylcyclohexene (**1**), and of several thiols to **1**, 1-chloro-4-*t*-butylcyclohexene (**3**), 1-methyl-(**4**), and 2-methyl-4-*t*-butylcyclohexene (**5**). The light-catalyzed addition of hydrogen bromide to **3** has been reported to give predominantly, *but not exclusively*, 2^c-chloro-5^t-*t*-butylcyclohexyl bromide,[8] and a bromine-bridged, radical intermediate nicely accommodated the data.[9] Sulfur-bridging has been invoked to rationalize the high degree of stereoselectivity observed in the addition of methanethiol to 1-chloro-4-*t*-butylcyclohexene (**3**).[10] Only two adducts were identified as products of the reaction between thiolacetic acid and 1-methyl-4-*t*-butylcyclohexene (**4**); the major isomer was that resulting from diaxial addition, namely 2^c-methyl-5^t-butylcyclohexanethiol acetate.[11] In methanethiol

(1) A preliminary communication describing a portion of the work has appeared: N. A. LeBel and A. DeBoer, *J. Amer. Chem. Soc.*, **89**, 2784 (1967).

(2) H. L. Goering, P. I. Abell, and B. F. Aycock, *ibid.*, **74**, 3588 (1952).

(3) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

(4) H. L. Goering, D. I. Relyea, and D. W. Larsen, *ibid.*, **78**, 348 (1956).

(5) F. G. Bordwell and W. A. Hewett, *ibid.*, **79**, 3493 (1957).

(6) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962). This article contains a comprehensive review of the stereochemistry of free radical additions.

(7) *Cf.* E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 219–227.

(8) The nomenclature system adopted by Curtin and Harder, *J. Amer. Chem. Soc.*, **82**, 2357 (1960), is utilized in this paper.

(9) P. D. Readio and P. S. Skell, *J. Org. Chem.*, **31**, 753 (1966).

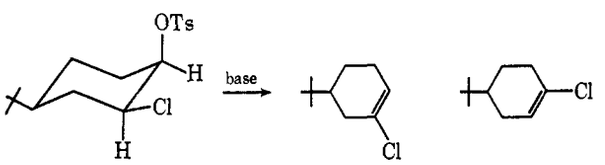
(10) P. D. Readio and P. S. Skell, *ibid.*, **31**, 759 (1966).

(11) F. G. Bordwell, P. S. Landis, and G. S. Whitney, *ibid.*, **30**, 3764 (1965).

additions to 4-*t*-butylcyclohexene and *trans*-Δ^2-octalin, the predominant adduct(s) resulted from axial attachment of the methanethiyl moiety.[12] In none of the cited recent studies[10-12] has a concentration or temperature effect upon the stereoselectivity of the thiol additions been noted, apparently contradicting the earlier observations.[4]

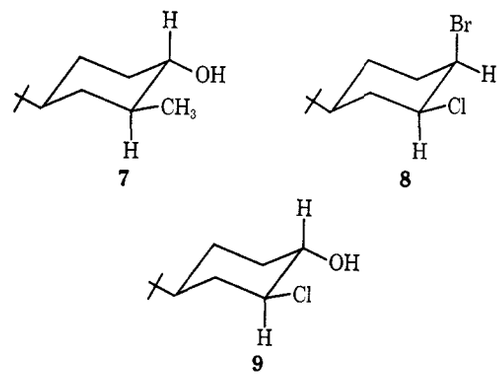
Starting Materials.—The vinyl chloride **1** was prepared in 85% yield by base-catalyzed elimination of 2^c-chloro-4^c-*t*-butylcyclohexyl tosylate (**2**). Both 1-chloro-4-*t*-butylcyclohexene (**3**)[9] and 1-methyl-4-*t*-butylcyclohexene (**4**)[11,13] were readily acquired. Catalytic hydrogenation of 2-methyl-4-*t*-butylphenol followed by dehydration of the mixture of cyclohexanols gave nearly equal amounts of the desired 2-methyl-4-*t*-butylcyclohexene (**5**) and the isomeric 1-methyl-3-*t*-butylcyclohexene (**6**). These compounds were separated by preparative gc. The structure of **5** was established *via* hydroboration followed by direct oxidation with chromic acid, which gave an 80:20 (*cis–trans*) mixture of the epimeric 2-methyl-4-*t*-butylcyclohexanones, as shown by gc and ir comparisons with an 85:15 mixture of authentic material.[14] The nmr spectrum of **5** very closely resembled that of **4**, and it is important to observe that the half band widths of the vinyl proton multiplets at δ 5.42 were identical in both cases (*ca.* 8.5 Hz).

The nmr spectrum of **6** indicated the presence of one olefinic proton (δ 5.40) and one methyl group attached to a double bond (δ 1.65). The narrower half band width (4.5 Hz) of the olefinic proton multiplet agrees with the proposed structure. Hydroboration followed by oxidation gave a very low yield of a 75:25 mixture of two ketones. The low yield is most readily explained in terms of a highly hindered olefinic group in **6**.



Hydrogenation of **5** and **6** over palladium–charcoal catalyst in ethanol gave mixtures of the *same two* isomeric hydrocarbons, as demonstrated by gc admixture. This mixture, containing the *cis*- and *trans*-1-methyl-3-*t*-butylcyclohexanes, was different from that obtained from the reduction of **4** (which gave a mixture, 80:20, of *trans*- and *cis*-1-methyl-4-*t*-butylcyclohexane, respectively).

It is of interest to note at this point that in the dehydration of the mixture of diastereomeric alcohols to give **5** and **6**, a substantial amount of 2^t-methyl-4^t-*t*-butylcyclohexanol (**7**) was recovered unreacted. A nmr spectrum permitted assignment of the axial stereochemistry (J = 22 Hz, δ 2.95) to the hydrogen α to the hydroxyl function.[15] The methyl group was assigned the equatorial position on the basis that oxidation with aqueous chromic acid in a water–ether system gave a ketonic product which showed an identical gc retention time to that of *cis*-2-methyl-4-*t*-butylcyclohexanone. Lithium aluminum hydride reduction of 2^t-methyl-4^t-*t*-butylcyclohexyl tosylate (**7**-OTs) gave a hydrocarbon whose ir spectrum identified it as *cis*-3-methyl-*t*-butylcyclohexane, and this material was indistinguishable from the major product obtained from the catalytic hydrogenation of **5** (*vide supra*).



Radical Additions and Product Identification.—When **1** reacted with hydrogen bromide in pentane solution, using benzoyl peroxide or ultraviolet light as initiators, a single bromochloride was detected by gas chromatography. The product was identified as 2^c-chloro-4^c-*t*-butylcyclohexyl bromide (**8**), resulting from a *trans*-diaxial addition. Evidence for the structure of **8** was based on its production in the reaction of phosphorous tribromide with the *trans,trans*-chlorohydrin **9** by way of an SN2 diplacement.[16] The measured dipole moment of **8**, 3.17 ± 0.04 D, is in excellent agreement with the *cis*- as well as the *trans*-diequatorial configuration of the halogen atoms.[17] The reaction of **8** with potassium *t*-butoxide to give only **1** provides further evidence for a Br-*a*, Cl-*e* configuration, and ir bands at 680 and 736 cm^{-1} confirm this assignment.

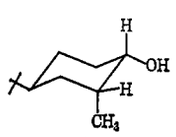
Both azobisisobutyronitrile- (AIBN) and ultraviolet light initiated additions of thiolacetic acid to **1** gave the *four* expected diastereomeric 2-chloro-4-*t*-butylcyclohexanethiol acetates **10–13**. The reactions were usually complete in 1 hr. The excess thiolacetic acid was removed by washing the reaction mixture with aqueous sodium bicarbonate solution. Control experiments in-

(12) (a) E. S. Huyser and J. R. Jeffrey, *Tetrahedron*, **21**, 3083 (1965); (b) E. S. Huyser, H. Benson, and H. J. Sinnige, *J. Org. Chem.*, **32**, 622 (1967).

(13) N. A. LeBel and G. G. Ecke, *ibid.*, **30**, 4316 (1965).

(14) N. L. Allinger and H. M. Blatter, *J. Amer. Chem. Soc.*, **83**, 994 (1961).

(15) The melting point of **7** has been reported as 72–73°, and that of i as 61–62°; F. Sipos, J. Krupicka, M. Tichy and J. Sicher, *Coll. Czech. Chem. Commun.*, **27**, 2079 (1962). The recovered alcohol, after recrystallization from pentane and sublimation at reduced pressure, had mp 61–62°, but on the basis of the chemical evidence offered it was assigned structure **7**. The reported melting points for **7** and i may have been inadvertently transposed, since the position of the nmr absorption band (δ 2.95) for the hydrogen α to the hydroxyl moiety in **7** agrees with that reported: E. L. Eliel, M. H. Gianni, Th. H. Williams, and J. B. Stothers, *Tetrahedron Lett.*, 741 (1962).



i

(16) E. L. Eliel and R. G. Haber, *J. Amer. Chem. Soc.*, **81**, 1249 (1959).

(17) P. Bender, D. L. Flowers, and H. L. Goering, *ibid.*, **77**, 3463 (1955).

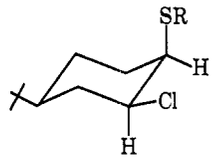
Table I

The Effect of Temperature and Acid Concentration on Product Distributions from Thiolacetic Acid Additions to 2-Chloro-4-*t*-butylcyclohexene (1).

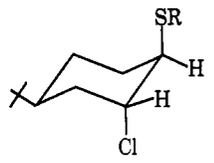
Run[a]	Molar ratio, AcSH: olefin	AcSH concn, *M*	Solvent (temp,[b] °C)	Composition, %[d] 10	11	12	13	Ratio (10 + 11): (12 + 13)	10:11	12:13
1	1:10	0.045	Hexane (5)[c]	57.9	5.1	24.8	12.2	1.7	11.4	2.0
2	1:10	0.1	Hexane (63)	47.0	7.6	30.0	15.5	1.2	6.3	1.9
3	1:1	1.0	Hexane (−60)[c]	78.7	1.6	12.8	6.9	4.1	49.2	1.9
4	1:1	0.45	Hexane (5)[c]	67.7	5.3	18.3	8.8	2.7	12.9	2.1
5	1:1	1.0	Pentane (37)	63.5	5.4	21.9	9.2	2.2	12.4	2.4
6	1:1	1.0	Hexane (63)	53.0	5.7	27.7	13.6	1.4	9.4	2.0
7	1:1	0.59	Heptane (86)	46.3	6.8	31.7	15.2	1.1	6.8	2.1
8	1:1	0.59	Heptane (106)	46.2	7.2	32.9	12.8	1.2	6.6	2.6
9	10:1	4.5	Hexane (5)[c]	74.6	5.7	13.1	6.5	4.1	13.0	2.0
10	10:1	5.9	Pentane (40)	70.8	4.6	17.4	7.3	3.1	15.5	2.4
11	10:1	5.9	Hexane (65)	60.5	7.6	20.6	11.4	2.1	8.0	1.8
12	10:1	5.9	Heptane (86)	56.8	6.9	24.9	11.3	1.8	8.2	2.2
13	10:1	5.9	Heptane (106)	53.5	6.6	28.0	11.8	1.5	8.1	2.4
14	30:1	13.5	None (5)[c]	75.8	5.4	12.0	6.8	4.3	14.0	1.8
15	30:1	10	Hexane (68)	63.7	5.1	21.5	9.6	2.2	8.2	2.0

[a] Reaction times were 1 hr. The reactions were run to 40–100% completion. Unless otherwise specified, AIBN was used as the initiator. [b] The reactions were carried out under an atmosphere of nitrogen. The temperature reported is that of the solution at reflux, except for runs 1, 4, 8, 9, 13, and 14, which were run in a sealed tube in a constant-temperature bath. Run 3 was carried out using a 2-propanol–Dry Ice bath. [c] Ultraviolet light was used as the initiator. [d] The reported percentages are normalized; the deviations observed from duplicate runs and multiple analysis were ±1.0% for **10** and **12** and ±0.5% for **11** and **13**.

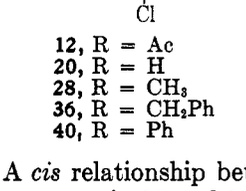
dicated that longer reaction times and the sodium bicarbonate washings did not change the relative proportions of products.



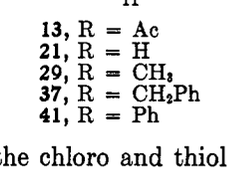
10, R = Ac
18, R = H
26, R = CH_3
34, R = CH_2Ph
38, R = Ph



11, R = Ac
19, R = H
27, R = CH_3
35, R = CH_2Ph
39, R = Ph



12, R = Ac
20, R = H
28, R = CH_3
36, R = CH_2Ph
40, R = Ph



13, R = Ac
21, R = H
29, R = CH_3
37, R = CH_2Ph
41, R = Ph

A *cis* relationship between the chloro and thiolacetoxy groups in **10** and **12** was strongly indicated by the fact that saponification and subsequent *re*acetylation of the chlorothiolacetate mixture afforded these as the sole chlorothiolacetates. The *trans* isomers **11** and **13** were expected to be converted to episulfides under these conditions, and chlorothiolacetates could not be regenerated upon reaction with acetic anhydride. When the adduct mixture was treated with a stoichiometric amount of sodium ethoxide in ethanol followed by the addition of excess methyl iodide, only two chloromethyl sulfides, **26** and **28**, were produced. These were formed in exactly the same ratio as that of **10**:**12** in the original mixture.

Additional support for the structural assignments of diastereomers **10**–**13** was obtained from the infrared and nmr spectra. Each isomer was separated by preparative gc and was examined independently. The band positions for the C–Cl stretching frequency were consistent with the respective configurations of the chloro substituents, and the observed nmr patterns unambiguously define the positions of the protons geminal to chlorine and to thiolacetoxy. For example, the distinction between **10** and **12** follows: for **12** the ir bands at 675 and 740 cm^{-1} indicated axial chlorine, and the nmr absorptions at δ 3.72 (1 H, $W_{1/2}$ = 21 Hz) and δ 4.50 (1 H, $W_{1/2}$ = 8 Hz) were consistent with an axial hydrogen α to thiolacetoxy and an equatorial hydrogen α to chlorine; the ir bands at 710 and 735 cm^{-1} in **10** are for equatorial chlorine, and the poorly resolved nmr multiplet at δ 3.78–4.58 (2 H) compared with the well-separated resonances in **12** results from upfield shift of the axial proton α to chlorine and a downfield shift of the equatorial proton α to thiolacetoxy. A 50-Hz scan of the acetyl methyl region [–$SCOCH_3$, δ 2.28–2.37] of the mixture of these chlorothiolacetates showed four distinct bands. In addition, the thiolacetate **11** was prepared by the reaction of *cis*-4-*t*-butylcyclohexene episulfide with acetyl chloride.

The radical-chain addition of thiolacetic acid to **1** was examined under varying reaction conditions, and reproducible concentration and temperature effects were observed as listed in Table I. The results of solvent dependency on the product distribution were also investigated, and these data are summarized in Table II.

The radical addition of thiolacetic acid to **3** to give the 2-chloro-5-*t*-butylcyclohexanethiol acetates **14**–**17** was also investigated in order to determine whether the position of the chlorine atom had any marked effect on the stereochemical consequences of the over-all addition process. The effects of concentration and temperature for these additions are shown in Table III.

A detailed structure proof of the chlorothiolacetates **14**–**17** was not undertaken. It was assumed that the gc elution order would be identical with that for the isomeric 2-chloro-4-*t*-butylcyclohexanethiol acetates (**10**–**13**). Saponification and subsequent methylation of the

TABLE II

PRODUCT DISTRIBUTIONS FROM THIOLACETIC ACID ADDITIONS TO 2-CHLORO-4-*t*-BUTYLCYCLOHEXENE (1) IN VARIOUS SOLVENTS

Run[a]	Molar ratio, AcSH: olefin	AcSH concn, *M*	Solvent (temp,[b] °C)	Composition, %[c] 10	11	12	13	Ratio (10 + 11): (12 + 13)	10:11	12:13
6	1:1	1.0	Hexane (63)	53.0	5.7	27.7	13.6	1.4	9.4	2.0
16	1:1	1.0	CS_2 (46)	56.4	6.6	25.0	12.0	1.7	8.6	2.1
17	1:1	1.0	Methanol (64)	49.5	7.2	27.9	15.4	1.3	6.9	1.8
18	1:1	1.0	C_6H_5Cl (67)	53.1	5.4	27.4	14.1	1.4	9.9	1.9
19	1:1	1.0	C_6H_5Cl (105)	46.4	6.7	31.5	15.3	1.1	7.1	2.1
11	10:1	5.9	Hexane (65)	60.5	7.6	20.6	11.4	2.1	8.0	1.8
20	10:1	5.9	CS_2 (45)	63.5	7.6	18.2	10.7	2.5	8.4	1.7
21	10:1	5.9	Methanol (63)	58.3	7.6	22.0	12.1	1.9	7.7	1.8
22	10:1	5.9	C_6H_5Cl (67)	64.7	5.6	19.3	10.4	2.4	11.6	1.9
23	10:1	5.9	C_6H_5Cl (98)	49.2	8.0	27.7	15.2	1.3	6.2	1.8
15	30:1	10	Hexane (68)	63.7	5.1	21.5	9.6	2.2	12.5	2.2
24	30:1	10	Methanol (66)	61.0	7.4	21.0	10.6	2.2	8.2	2.0

[a] Runs 6, 11, and 15 are from Table I and are included here for comparison. Reaction times were 1 hr. The reactions were run to 40–100% completion. AIBN was used as the initiator. [b] The reactions were carried out under an atmosphere of nitrogen. The temperature reported was that of the solution at reflux except for runs 18 and 22, which were run at an oil-bath temperature of 67°. [c] The reported percentages are normalized; the deviations observed from duplicate runs and multiple analysis were ±1.0% for **10** and **12** and ±0.5% for **11** and **13**.

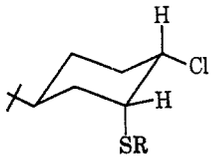
TABLE III

THE EFFECT OF TEMPERATURE AND ACID CONCENTRATION ON PRODUCT DISTRIBUTIONS FROM THIOLACETIC ACID ADDITIONS TO 1-CHLORO-4-*t*-BUTYLCYCLOHEXENE (3)

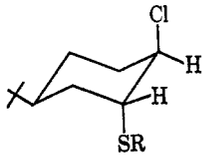
Run[a]	Molar ratio, AcSH: olefin	AcSH concn, *M*	Temp,[b] °C	Composition, %[c] 14	15	16	17	Ratio (14 + 15): (16 + 17)	14:15	16:17
25	1:1	1.0	−60	74.4	1	14.2	10.4	3.1	74	1.4
26	1:1	1.0	63	52.8	4.3	24.4	18.5	1.3	12.3	1.3
27	10:1	5.9	65	61.3	4.5	19.8	14.8	1.9	13.6	1.3

[a] Reaction times were 1 hr. Ultraviolet light was used as the initiator for run 25. AIBN was used to initiate runs 26 and 27. [b] A 2-propanol–Dry Ice bath was used to cool the reaction vessel in run 25. The temperatures reported for runs 26 and 27 were that of the solution at reflux. All runs were carried out under an atmosphere of nitrogen. Hexane was the solvent. [c] The reported percentages are normalized. The data reported for run 25 is based on one run only. Those reported for runs 26 and 27 are based on duplicate runs and multiple analysis. The observed deviations were ±1.0% for **14** and **16**, and ±0.5% for **15** and **17**.

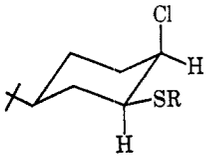
adduct mixture **14–17** gave two methyl sulfides, **30** and **32**, in the same ratio determined for **14**:**16** in the original mixture, supporting the structural assignments of the *cis* compounds.



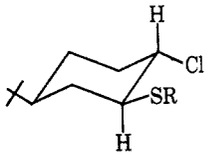
14, R = Ac
22, R = H
30, R = CH_3



15, R = Ac
23, R = H
31, R = CH_3



16, R = Ac
24, R = H
32, R = CH_3



17, R = Ac
25, R = H
33, R = CH_3

The possibility that any of the 2-chloro-5-*t*-butylcyclohexanethiol acetates **14–17** could have been formed during the addition of thiolacetic acid to 2-chloro-4-*t*-butylcyclohexene or during the analysis of the adducts **10–13** (by a molecular rearrangement process) was eliminated by gc analysis of the admixture of both series of chlorothiolacetates. Eight distinct peaks were observed.

Determination of the product distributions from the free-radical additions of hydrogen sulfide to **1** and **3**, which would give the chlorothiol adducts **18–21** and **22–25**, respectively, was complicated both by a lack of resolution and by partial decomposition on gc analysis. Therefore, these thiols were treated with acetic anhydride and a catalytic amount of pyridine; and the corresponding thiolacetates were produced in quantitative yield. Analyses of the thiolacetates permitted the quantitative results shown in Tables IV and V.

The addition of methanethiol to 1-chloro-4-*t*-butylcyclohexene (**3**) to give the mixture of adducts **30–33** has been studied by Readio and Skell, and the distribution was ascertained primarily from the results of solvolysis studies.[10] It was found that nmr spectroscopy provided a superior method of determining the amount of each diastereomer formed. This technique was first applied to the 2-chloro-5-*t*-butylcyclohexyl methyl sulfides (**30–33**). A 50-Hz scan of the $-SCH_3$ region (δ 2.07–2.22) afforded a series of well-defined singlets, and the integrated areas beneath each band provided a measure of the relative amounts of the respective adducts. Diastereomers **30** and **32** were collected by preparative gc and their nmr spectra agreed with those already published. The diaxial chlorosulfide **31** was synthesized from *cis*-4-*t*-butylcyclohexene oxide *via* reaction with sodium thiomethoxide followed by treatment with thionyl chloride in pyridine. The nmr spectrum supported the diaxial arrangement and the infrared spec-

Table IV

Product Distributions from Thiol Additions to 2-Chloro-4-*t*-butylcyclohexene (1)

Run[a]	Temp, °C	Molar ratio	Composition, %[b]			
Hydrogen Sulfide, R = H						
28[c]	5	12:1	**18**, 78.9	**19**, 2.2	**20**, 8.9	**21**, 10.0
Methanethiol, R = CH_3						
33[c]	5	1:1	**26**, 77	**27**, 5	**28**, 8	**29**, 10
34[c]	5	10:1	**26**, 82	**27**, 5	**28**, 6	**29**, 7
35[d]	86	1:1	**26**, 63	**27**, 9	**28**, 15	**29**, 14
Benzyl Mercaptan, R = CH_2Ph						
36[c]	10	1:1	**34**, 71	**35**, 10	**36**, 11	**37**, 8
37[d]	86	1:1	**34**, 61	**35**, 12	**36**, 20	**37**, 7
Thiophenol, R = Ph						
50[e]	80	2:1	**38**, 80	**39**, 2	**40**, 14	**41**, 4

[a] Reaction times were 1 hr, except for run 50 which was allowed to proceed for 12 hr. The solvent was hexane, except in run 50 where no solvent was employed. [b] Percentages are normalized and are based on the analytical methods described in the text. [c] Uv initiation. [d] AIBN initiation. [e] Benzoyl peroxide initiation.

Table V

Product Distributions from Thiol Additions to 1-Chloro-4-*t*-butylcyclohexene (3)

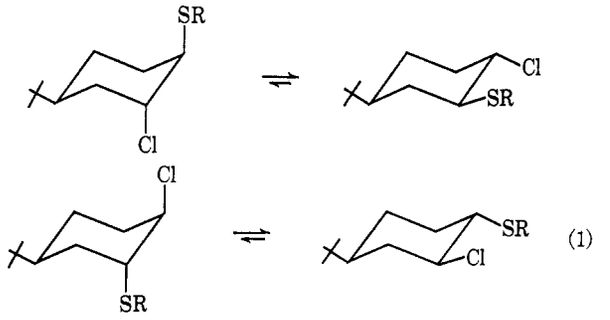
Run[a]	Temp, °C	Molar ratio	Composition, %[b]			
Hydrogen Sulfide, R = H						
29	*ca.* −50	10:1	**22**, 71.3	**23**, 1.2	**24**, 9.3	**25**, 18.2
Methanethiol, R = CH_3						
30[c]	−78	2.3:1	**30**, 88–91	**31**, 2.5	**32**, 2	**33**, 7–10
31	−60	*ca.* 3:1	**30**, 89	**31**, 2	**32**, 3	**33**, 6
32	10	*ca.* 3:1	**30**, 79	**31**, 4	**32**, 6	**33**, 11

[a] Reaction times were 1 hr; uv initiation was used and a nitrogen atmosphere was maintained over the solutions. [b] Percentages are normalized. [c] Data from ref 10.

trum showed a band corresponding to an axial chlorine–carbon stretching mode (685 cm^{-1}). 2-Chloro-4-*t*-butylcyclohexyl methyl sulfide (**27**) was prepared by a similar method from *trans*-4-*t*-butylcyclohexene oxide. The nmr and ir spectra again supported the assigned diaxial configuration.

Assignment of the position of the $-SCH_3$ absorption of **30**, **31**, **32**, and **27** was done by observing enhancement in the intensity of the respective nmr band upon successive addition of each component to the mixture. The position of the $-SCH_3$ resonance for the diequatorial compound **33** was based on the fact that, when the mixture of **30**–**33** was heated at 76° in a sealed nmr sample tube, a new band assignable to **27** appeared at the expense of **33**. The thermal equilibrium **33** ⇌ **27** is an example of the now well-established "generalized diaxial–diequatorial rearrangement" (eq 1).[18]

A similar pattern was observed in the nmr spectrum of the 2-chloro-4-*t*-butylcyclohexyl methyl sulfides **26**–**29** obtained from addition of methanethiol to **1**. The position of the $-SCH_3$ resonance for the two *cis* diastereomers **26** and **28** was determined from a mixture of the two sulfides obtained by saponification and methylation of the mixture of the analogous chlorothiolacetates **10**–**13**. The method employed for the identification of the $-SCH_3$ band of **33** was used to assign the band to **29** (*i.e.*, **29** ⇌ **31** on heating). Tables IV and V summarize the results of methanethiol additions to both 1- and 2-chloro-4-*t*-butylcyclohexene. The relative proportions reported for runs 31 and 32 were obtained by removing significant amounts of **30** by crystallization at −20° and obtaining a weight per cent of this material. Concentration of the mother liquors and nmr analysis of the remaining sulfides permitted calculation of the initial product distribution. The major *cis* isomer **34** would not crystallize, and hence it was impossible to procure any reasonable quantitative data for the addition of methanethiol to 2-chloro-4-*t*-butylcyclohexene (**1**) at −60°.



(1)

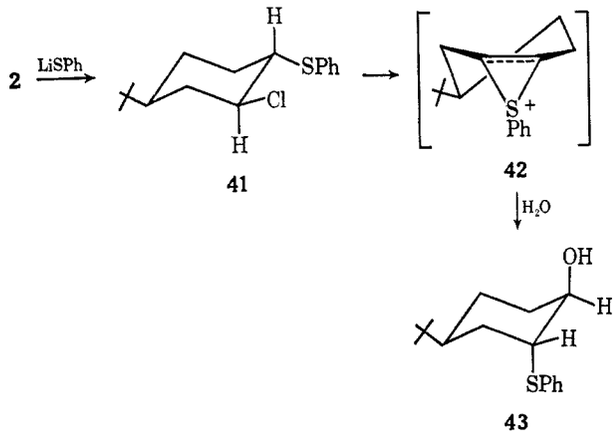
Free-radical addition of benzyl mercaptan to **1** produced the diastereomeric 2-chloro-4-*t*-butylcyclohexyl benzyl sulfides **34**–**37**. The relative proportion of each isomer was determined by examining the benzyl proton region (δ 3.57–3.91) of the nmr spectra. The results are also listed in Table IV. A mixture of the two *cis* isomers **34** and **36** was obtained from a chlorothiolacetate mixture (**10**–**13**) by saponification and subsequent treatment with benzyl iodide. The diaxial benzyl sulfide **35** was prepared by the method used for the synthesis of the diaxial methyl sulfide **27**. The nmr spectrum supported a diaxial arrangement of the chloro and benzylsulfo groups in this isomer. The position of the benzyl proton absorption of **37** (diequatorial) was determined by synthesizing 2^t-chloro-5^t-*t*-butylcyclohexyl benzyl sulfide. Heating this material produced a mixture containing *ca.* 70% **37**.

The benzoyl peroxide catalyzed addition of thiophenol to **1** (2:1 molar ratio) gave, after recovery of starting vinyl chloride, a 35% yield of a 1:1 adduct. The infrared spectrum of the purified adduct was very similar to that of the *cis,cis*-chlorosulfide **38** (*vide infra*). Consequently, solvolytic studies were employed for an analysis. It had been previously determined that solvolysis of pure **38** in 80% aqueous ethanol at reflux temperature for 24 hr gave no detectable chloride. Solvolysis of the adduct gave 6–7% titratable chloride, suggesting the presence of a *trans* isomer. The solvolysis product (this preparative reaction was carried out in 70% acetone) was separated from unreacted **38** by chromatography and was found to consist of a mixture of 73 ± 5% 2^t-phenylsulfo-4^c-*t*-butylcyclohexanol (**43**) and 27 ± 5% of 2^t-phenylsulfo-5^t-*t*-butylcyclohexanol by infrared analysis. The crystalline *p*-nitrobenzoate of **43** could be isolated from the mixture. The purified major adduct **38** was shown to be at least 85% homogeneous by nmr analysis—some contamination by another *cis* isomer was apparent. Similar results were obtained when the addition reaction was carried out

(18) A recent report describes such processes in steroidal systems: J. F. King, K. Abikar, D. M. Deaken, and R. G. Pews, *Can. J. Chem.*, **46**, 1 (1968).

with a 10:1 molar ratio of thiophenol to olefin, except that only 4–5% *cis* addition was detected by the solvolysis studies.

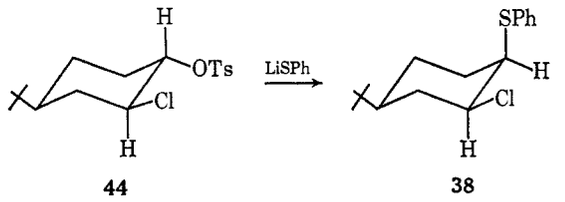
The syntheses of the thiophenol adducts **38**, **39**, and **41** were undertaken. When a suspension of lithium (or sodium) thiophenolate was stirred with the tosylate **2** in tetrahydrofuran at 40–60°, a 60% yield of 2^t-chloro-4^t-*t*-butylcyclohexylphenyl sulfide (**41**) was obtained. Substantial amounts of **1** and diphenyl disulfide were also isolated. The structure of **41** was confirmed as follows. The *trans* orientation of the chloride and sulfide groups was readily determined by the fact that **41** underwent facile solvolysis—in fact, on attempted alumina chromatography. This solvolysis, more likely than not, proceeds initially through a twist form to give the intermediate **42**. This sulfonium ion



would react with water to give 2^t-phenylsulfo-4^c-*t*-butylcyclohexanol (**43**)—the expected product of diaxial ring opening. Compound **43** was also prepared by reaction of *cis*-4-*t*-butylcyclohexene oxide with sodium thiophenolate and was desulfurized to *cis*-4-*t*-butylcyclohexanol. The nmr spectrum of **41** was consistent with its configuration assignment.

Ultimate purification of **41** is complicated by the possibility of diaxial–diequatorial rearrangement to 2^t-chloro-5^t-*t*-butylcyclohexyl phenyl sulfide. Repeated distillation of **41** did, in fact, cause increasing contamination by an isomer, determined by nmr. However, the structure of **41** was further verified by oxidation to a crystalline sulfone which underwent facile dehydrochlorination to 1-phenylsulfono-4-*t*-butylcyclohexene.

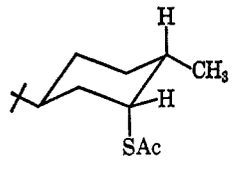
The displacement reaction with thiophenolate and the *trans,trans*-tosylate **44** led to the formation of 2^c-chloro-4^c-*t*-butylcyclohexylphenyl sulfide (**38**) in low

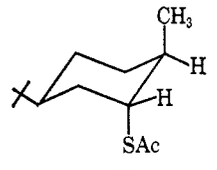


yield. The structure assigned to **38** is supported by the ir and nmr spectra and by its resistance to solvolysis. The chloro sulfone obtained from **38** also gave 1-phenylsulfono-4-*t*-butylcyclohexene on treatment with base.

2^t-Chloro-4^c-*t*-butylcyclohexylphenyl sulfide (**39**) was synthesized by the method analogous to that used for the preparation of **27**. The intermediate hydroxy sulfide could be desulfurized to *trans*-3-*t*-butylcyclohexanol.

The free-radical addition of thiolacetic acid to 1-methyl-4-*t*-butylcyclohexene (**4**) has been reported by Bordwell and coworkers.[11] Only two products were identified, and concentration and temperature effects were apparently not observed. The work has been repeated in this study, and *three* 2-methyl-5-*t*-butylcyclohexanethiol acetates (**45**, **47**, **48**) have been detected by





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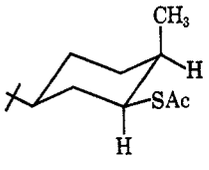
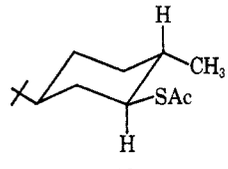




gc and nmr analysis. A 50-Hz scan of the acetyl methyl region (δ 2.20–2.30) of the nmr spectrum showed three singlets. Surprisingly, a unique concentration effect was observed, as can be seen from examination of the data in Table VI.

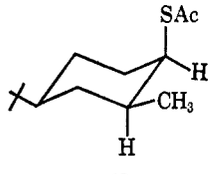
TABLE VI
PRODUCT DISTRIBUTIONS FROM THIOLACETIC ACID ADDITIONS TO 1-METHYL-4-*t*-BUTYLCYCLOHEXENE (**4**)

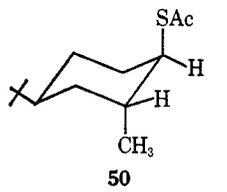
Run[a]	Molar ratio,[b] AcSH: olefin	Composition, %[c] 45	48	47
38	1:10	79.9	15.9	4.2
39	1:1	80.4	17.5	2.1
40	10:1	74.0	22.4	4.2
41	30:1	71.6	23.4	5.0

[a] Reaction times were 1 hr. The reactions were run in hexane at 86° in sealed tubes. AIBN was used as the initiator. [b] The olefin concentration was 0.45 *M* in all cases. [c] The reported percentages are normalized, and are the average of two runs.

Structure proof of the major products **45** and **48** was reported.[11] Structure **47** is suggested for the minor adduct (*vide infra*).

The free-radical addition of thiolacetic acid to 2 methyl-4-*t*-butylcyclohexene (**5**) was also investigated. Only three 2-methyl-4-*t*-butylcyclohexanethiol acetates (**49**, **51**, **52**) were observed by gc and nmr analysis.





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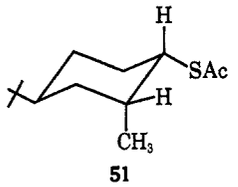
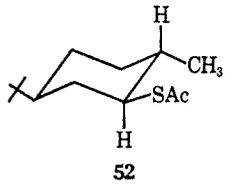




A concentration effect similar to that observed for the thiolacetic acid addition to **4** was noted. The effect of reaction temperature was studied, and both sets of data are shown in Table VII.

Table VII

Product Distributions from Thiolacetic Acid Additions to 2-Methyl-4-*t*-butylcyclohexene (**5**)

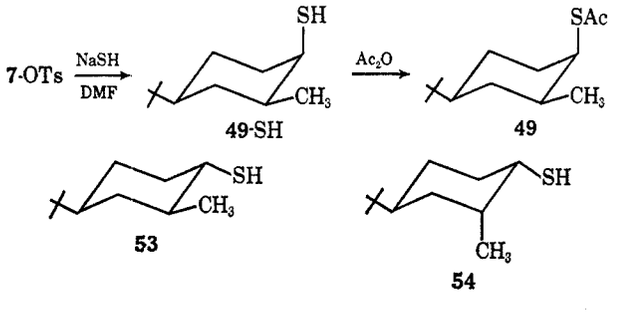
Run[a]	Temp, °C	Molar ratio,[b] AcSH: olefin	Composition, %[c] 49	52	51
42	86	1:10	84.2	14.0	1.8
43	−60	1:1	63.8	32.7	3.5
44	5	1:1	79.3	18.1	2.7
45	86	1:1	79.7	17.9	2.4
46	5	10:1	66.5	28.3	4.7
47	86	10:1	73.9	20.7	5.5
48	5	30:1	64.7	28.9	6.4
49	86	30:1	71.4	23.3	5.4

[a] Reaction times were 1 hr. Hexane was the solvent, and the reactions were run in sealed tubes. AIBN initiation was used for the runs at 86°, and ultraviolet light initiation for the remaining runs. [b] Solutions were 0.45 *M* in olefin in all cases. [c] Reported percentages are normalized, and runs 42, 45, 47, and 49 are averages of two or more reactions.

Since the amounts of *trans*-diaxial products resulting from thiolacetic acid additions to the chloro olefins **1** and **3** remained fairly constant over a wide range of thiol/olefin ratios, and since the minor product from thiolacetic acid addition to **5** showed a general tendency to be formed in increasing amounts with higher ratios of thiol:olefin, **51** was assigned the *cis* (*e*-SAc, *a*-CH_3) structure. Even though a sufficient number of reactions with thiolacetic acid and **4** were not carried out so that a similar trend for the minor product could be established, **47** was assigned the *cis* (*e*-SAc, *a*-CH_3) structure because of the similarity between the two systems. Evidence for the presence of a fourth adduct (*e.g.*, **46** and **50**) could not be found.

The minor adduct may have resulted from ionic addition of thiolacetic acid to **5**. However, examination of the literature indicated that such reactions are unusual and occur in a few special cases only if oxygen has been rigorously excluded from the reaction mixture. Attempts to promote ionic addition of thiolacetic acid to **5**, *i.e.*, addition of a radical inhibitor or addition of *p*-toluenesulfonic acid, produced small amounts of two products, presumably adducts resulting from ionic addition, in addition to the adducts **49**, **51**, and **52**. The proportion **51**:(**49** + **52**) did not increase under conditions that should promote ionic additions, which suggests that **51** is formed by a free-radical process.

An authentic sample of diastereomer **49** was prepared by a S_N2 displacement reaction of the diequatorial tosylate **7**-OTs with sodium hydrosulfide in dimethylformamide followed by acetylation of the thiol with acetic anhydride. The nmr spectrum of **49** showed the presence of an equatorial hydrogen geminal to the –SAc group ($W_{1/2}$ = 8 Hz, δ 3.83). The synthesized material showed the same gc retention time and infrared spectrum as the sample of **49** separated from the mixture by preparative gc.



The stereochemistry at the carbon atom bearing the thiolacetoxy moiety in **52** was assigned on the basis of the nmr spectrum ($W_{1/2}$ = 25 Hz, δ 2.93) of a sample obtained by preparative gc. The equatorial position of the methyl groups in both **49** and **52** was established by Raney nickel disulfurization of a mixture of **49**, **51**, and **52** (in the proportions described in run 45, Table VII). A mixture of the thiols **49**-SH, **53**, and **54** was obtained from saponification of the corresponding thiolacetates (**49**:**52**:**51** = 73.3:20.8:5.7), and these were also desulfurized. Both reductions showed a 90:10 ratio (based on gc) of *cis*- and *trans*-1-methyl-3-*t*-butylcyclohexane, respectively. Obviously the *cis* hydrocarbon could only have arisen from **49** and **52** and **49**-SH and **53**; and, therefore, the two isomers **49** and **52** *must have been present* to the extent of at least 90% in the original adduct.

The relative rates of addition of thiolacetic acid to 2-chloro- and 2-methyl-4-*t*-butylcyclohexene (**1**, **5**) were calculated on the basis of results obtained from a competition experiment. A hexane solution of **1**, **5**, and thiolacetic acid in the proportion 1:1:0.9, respectively, was irradiated at 10° for 1 hr. Analysis of the starting olefins by gc, after compensating for differences in thermal response factors, and calculation showed that **5** reacted 34 times faster than did **2**.

Discussion

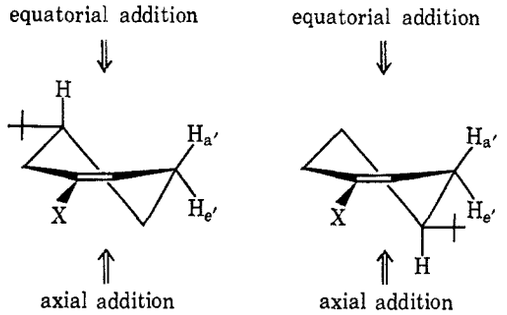
The radical-chain addition of hydrogen bromide to 2-chloro-4-*t*-butylcyclohexene (**1**) proceeds to give exclusively the product **8** from *trans*-diaxial, *anti*-Markovnikov addition. Similarly, addition to the isomeric vinyl chloride **3** gave predominantly the analogous type of product,[9] and we find no compelling reason not to accept the bridged bromoalkyl radical hypothesis[9] to account for the results in both systems. Significantly, the higher stereoselectivity for axial attachment of the addendum radical (Br· in the case of hydrogen bromide) in additions to the 2-halo-4-*t*-butylcyclohexenes as compared to the 1-halo analogs appears to be a general phenomenon, since it is also observed with thiol additions to **1** and **3**. Some subtle conformational factor is probably responsible.

As is apparent from the tabulated results, thiol concentration and temperature significantly affect the relative proportions of products formed in the additions of thiols to the four olefins used in this study. The concentration dependence is dramatically demonstrated by comparison of runs 1, 4, 9, and 14 in Table I, runs 44, 46, and 48 in Table VII, and runs 33 and 34 in Table IV.

The previous report of the dependence of the *cis*:*trans* adduct ratio upon thiolacetic acid concentration in free-radical additions to 1-chlorocyclohexene has been attributed to the effective competition between chair–chair interconversion of the intermediate radical and chain transfer.[4] It was rationalized that increasing the

thiol concentration would shorten the lifetime of the initially formed 2-axial thiyl-1-chlorocyclohexyl radical (which was assumed to undergo chain transfer to give only *cis* adduct), thereby slowing its rate of conversion into the 2-equatorial thiyl-1-chlorocyclohexyl radical (which was said to undergo chain transfer to give both *cis* and *trans* adducts).[4] *This explanation cannot be valid for a t-butylcyclohexyl system.*

An alternative explanation must be sought for the effects delineated in this work. The *t*-butyl groups in olefins **1**, **3**, **4**, and **5** should not directly interfere with the direction of approach (top or bottom) of the thiyl radical to the double bond, and exclusive *anti*-Markovnikov orientation is observed in the additions.

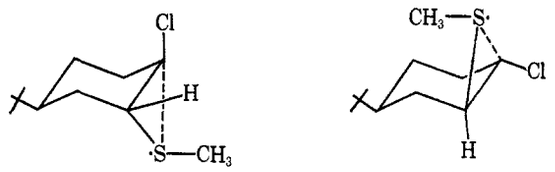


1, X = Cl
5, X = CH_3

3, X = Cl
4, X = CH_3

Over-all preference for axial orientation of the attacking thiyl group is observed in all addition reactions studied. One explanation for this prevalence for axial attack[19] by a thiyl radical is that the pseudoaxial hydrogens ($H_{a'}$) hinder the approach of the incoming group. In fact, steric approach control has been suggested as being partially responsible for the direction of thiyl-radical attack in the addition of thiolacetic acid to 1-methyl-4-*t*-butylcyclohexene.[11] However, there is a marked preference for axial addition of the thiolacetoxy radical to the Δ^5 double bonds of steroids.[20] Approach from the β side (axial attack) is generally regarded as sterically prohibitive, and thus it appears that steric hindrance is not the dominating factor in controlling the direction of radical addition to a cyclohexene.

An asymmetric sulfur-bridged radical **55** (R = CH_3) has been invoked to explain the high degree of stereoselectivity obtained in methanethiol additions to 1-chloro-4-*t*-butylcyclohexene (**3**).[10] The chloromethyl sulfide **30** (*a*-SCH_3, *e*-Cl; *trans* addition) comprised 86% of the adduct. The preponderance of axial over equatorial methylsulfo groups in the adduct was attributed to the difference in the activation energies required to produce intermediate **55** (axial thiyl-radical attack) and the bridged species **56** (equatorial thiyl-radical attack). It was suggested that *most* of the product **30** arises by direct chain-transfer with **55**. However, the presence of the three remaining 2-chloro-5-*t*-butylcyclohexyl methyl sulfides (**31**, **32**, and **33**) in the product mixture was rationalized by postulating an equilibration of the bridged-radical intermediates **55** and **56** with classical



55 **56**

open-chain radicals which, when followed by axial and equatorial chain transfer, would form a mixture of all four diastereomeric adducts **30–33**. These investigators also reported that no observable effect of concentration on product ratio was detected by varying the methanethiol concentration from 2.8 *M* to 14 *M*.[10]

Even if, as suggested,[10] bridged radicals are formed initially during radical additions of thiols to olefins, available evidence overwhelmingly points to the fact that such intermediates are not involved in the product-determining steps. For example, the highly stereoselective processes of *cis* additions of *p*-thiocresol to norbornene and to substituted norbornenes prohibit the intervention of a bridged species in the chain-transfer step.[21] Additionally, if a bridged radical such as **55** contributed significantly to the relative proportions of final products, then a change in the electron-donating or electron-withdrawing ability of the R group on the sulfur atom should have resulted in a noticeable effect on the stereochemical outcome of the reaction. An increasing interaction between the sulfur atom and the radical center due to the greater electron-donating capability of the R group should generate a proportionate increase in *trans*-diaxial addition.

The present work supplies data on the basis of an anticipated increasing electron-donating ability by the RS– group in the order thiolacetyl < thiyl < methanethiyl, and a bridged thiyl radical is not supported. From additions to 1-chloro-4-*t*-butylcyclohexene (**3**) at −60° (run 25 in Table III, runs 29 and 31 in Table V), the ratio of *cis* products (*a*-SR, *e*-Cl) to diaxial *trans* products is constant within experimental error (**14**:**15** = 74, **22**:**23** = 59, **30**:**31** = 45). Free radical additions of thiolacetic acid *and* of methanethiol to 2-chloro-4-*t*-butylcyclohexene at 5° (run 4 in Table I and run 33 in Table IV) also gave similar ratios of *cis* products to diaxial *trans* products (**10**:**11** = 13, and **26**:**27** = 15).

If bridged radicals are not important, other factors must be responsible for the high stereoselectivity. The marked preference for formation of *cis* product relative to *trans* product can best be explained—ignoring temporarily the high incidence of axial attack—by formation of the intermediate axial radical **57**. The steric shielding and possible dipolar repulsion provided by the axial –SR substituent located adjacent to the radical center should force the incoming thiol chain-transfer agent to approach in the direction opposite to this group. If this directive effect is superimposed on the established[11,22] preferential axial chain transfer which

(19) "Axial" and "equatorial" attack are technically misnomers. The axial or equatorial position of the thiyl radical is not known until after addition is complete. The term "parallel attack" has been suggested for approach to the cyclohexene double bond from the same side as the pseudoaxial hydrogen ($H_{a'}$). "Antiparallel attack" would then describe the approach from the other side: J. Valls and E. Toromanoff, *Bull. Soc. Chim. Fr.*, 758 (1961).

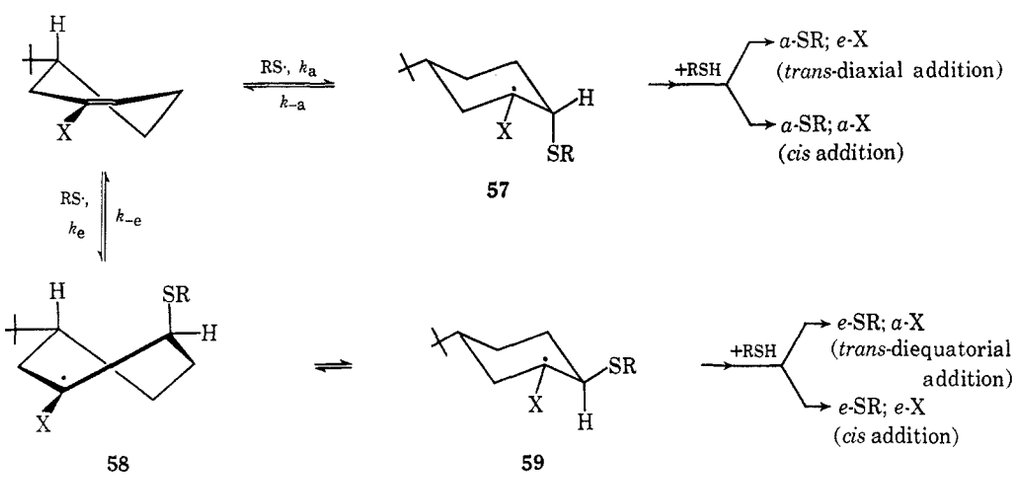
(20) R. M. Dodson, P. B. Sollman, and J. R. Deason, *J. Org. Chem.*, **30**, 2009 (1965); C. W. Shoppee, M. I. Akhtar, and R. E. Lack, *J. Chem. Soc.*, 877 (1964).

(21) A good summary is given by D. I. Davies and S. J. Cristol in "Advances in Free Radical Chemistry," Vol. I, G. H. Williams, Ed., Academic Press, Inc., New York, N. Y., 1965, Chapter 5.

(22) F. D. Greene, C. C. Chu, and J. Walia, *J. Org. Chem.*, **29**, 1285 (1964). See also F. R. Jensen, L. H. Gale, and J. E. Rogers, *J. Amer. Chem. Soc.*, **90**, 5793 (1968).

other cyclohexyl radicals undergo, the formation of substantial amounts of *cis* product from diaxial addition is not at all surprising.

As noted above, the ultraviolet light and AIBN-initiated additions of thiolacetic acid, hydrogen sulfide, and methanethiol to **1** and **3–5** led to products in which the relative proportions of adducts having the thiyl group in an axial position was greater than that with the thiyl group in an equatorial position. The initial preference is at least 9:1 and may be greater. A simple rationale is available to account for this type of "stereoelectronic control" of addition. Axial attack by a thiyl radical on 2-chloro-4-*t*-butylcyclohexene (**1**) will lead directly to a cyclohexyl radical having the chair conformation. Attack from the other side, the "equatorial direction," must give a twist-boat radical intermediate (**58**, X = Cl). The difference between the chair and twist-boat forms of cyclohexanone has been calculated as 3.205 kcal/mol.[23] If we assume that there is a similar energy difference between the two radical intermediates **57** and **58** (X = Cl), the rate of formation of **57** should be faster than that of **58**. Since the activation energy difference between chain transfer from the two intermediates is probably small, the preference for axial addition is best explained in terms of the lower energy transition state required to form the chair intermediate **57**. The magnitude of the difference also depends on the position of the transition state on the reaction coordinate. For an exothermic reaction, *e.g.*, **1** + RS· → **57**, the transition state undoubtedly more closely resembles starting material than products.



It is generally agreed that the rate-determining step in free-radical additions of thiols to alkenes is chain transfer, and that the addition of thiyl radicals to olefins is reversible. The extent of reversal is a function of both olefin and radical stability, because both are associated with the relative free energies of the intermediate states. However, elimination of thiyl radical requires a geometry in which the p orbital of the trigonal radical center is colinear with the appropriate orbital of the developing adjacent trigonal center. This requirement is met in the initially formed intermediates **57** and **58**, but, for elimination of a thiyl radical to occur from intermediate **58**, the twist conformation must be maintained. It is very likely that **58** is converted to the lower energy chair conformation **59**. The conformational energy differences between axial and equatorial –SH and –SCH_3 groups are approximately 0.7 kcal/mol;[24] hence it is reasonable to expect that the intermediate **59** (*e*-SR) would be more stable than **57** (*a*-SR). The energy of activation for the reversal process **59** → **1** + RS· is thus expected to be greater than that for **57** → **1** + RS·.

At low thiol to olefin ratios, reversal of the initial axial thiyl radical attack competes favorably with chain transfer. More of the adducts with equatorial SR groups will be detected because of higher conversion to intermediate **59**. Some chain transfer may occur from **58** leading to products having the skew-boat conformation, which would then undergo conformational inversion to the more stable chair forms. However, the equilibrium **58** ⇌ **59** favors **59**, and it is not unreasonable to predict that chain transfer would occur only from **59**. At high thiol to olefin ratios, the rate of the bimolecular chain transfer reaction is increased, and a higher proportion of the kinetically formed intermediate **57** will be trapped. This increase in the relative proportion of the adducts having axial –SR groups accompanying an increase in thiol concentration can only be explained on the basis that the lifetime of intermediate **57** is shortened, slowing down the competing process of elimination to olefin and thiyl radical. It is by this inhibition of reversibility of the addition step that high thiol concentration exerts its dominant control over the overall stereoselectivity of the reaction. Chain transfer from the axial thiyl radical intermediate **57** is much more highly selective in giving *trans* addition than is transfer from **59**. We are inclined to believe that the influence of low thiol concentration in reducing the *trans:cis* addition ratio *via* **57** is only of secondary importance.

One fact that has not been accounted for as yet is that additions of methanethiol are more highly stereoselective than free-radical additions of thiolacetic acid. It was pointed out earlier that the extent of reversal in the addition step is a function of both olefin stability and radical stability. In the system under study, the olefin is the same but the relative stabilities of the thiolacetoxy and methanethiyl radicals differ. The stabilities of the intermediates **57** should be the same whether R = Ac or R = CH_3. Because of the greater stability of the thiolacetoxy radical (relative to the methane-

(23) Personal communication from Professor N. L. Allinger.

(24) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 438.

thiyl radical), the reversal process, **57** → **1** + RS· (R = Ac), is more facile than if R = CH_3. This difference in the degree of reversibility of the addition step must be responsible for the observed variation in the degree of stereoselectivity. If the chain-transfer rate had been the determining factor ($CH_3COSH > CH_3SH$), then the opposite order of stereoselectivity would have been noted. The stereospecificity of hydrogen bromide additions can also be included in the over-all scheme if one considers that no reversibility of the addition step occurs because of the very high rate of chain transfer for HBr.

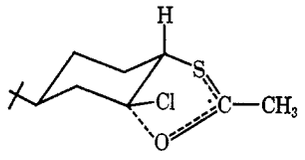
The decrease in stereoselectivity observed with an increase in temperature is also consistent with the scheme presented for additions of thiols to **1**. A higher temperature increases the probability that reaction will occur *via* the higher energy process (**1** → **58**) as well as favoring reversal from **57**. Both effects result in an over-all accumulation of products from the thermodynamically more stable intermediate **59**.

Special solvent effects could have been responsible for controlling the stereochemical outcome of the thiol-addition reactions. However, the data in Table II indicate that each of the observed trends—such as preferred direction of chain transfer from the intermediate cyclohexyl radical, thiol concentration effects, and the effect of temperature—cannot be attributed solely to the nature of the solvent, since these trends are in the same direction and are about the order of magnitude in solvents of widely different polarity.

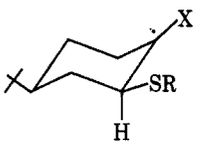
Displacement with the 2-equatorial thiyl-substituted cyclohexyl radical (**59**, X = Cl) is apparently not a very selective process. Chain transfer from **59** (chair conformation) will proceed through transition states in which the stereochemical relationship between the equatorial thiyl substituent, the chlorine group, and the chain-transfer agent HSR is approximately the same. Although the conformational free-energy difference between the developing axial and equatorial orientations of chlorine cannot be neglected, this is only 0.4 kcal/mol in the fully developed product,[24] and is not large enough to cause one transition state to be greatly favored over the other.

There is one intriguing aspect of the stereoselectivity in chain transfer from intermediate **59** (X = Cl). A rather surprising change was noted in the ratio of *trans* addition (*e*-SR, *a*-Cl) to *cis* addition (*e*-SR, *e*-Cl) on variation of the addendum from thiolacetic acid to hydrogen sulfide and methanethiol, although in none of the examples cited was the process very stereoselective. The ratio of equatorial to axial chain transfer from **59** (*e*-SR, R = Ac) during the free-radical addition of thiolacetic acid to **1** was fairly constant at 2:1 throughout the range of acid concentrations and temperatures investigated (**12**:**13** in Table I). This stereoselectivity observed in chain transfer from **59** has virtually disappeared in additions of hydrogen sulfide and methanethiol. A similar change in stereoselectivity with different thiols was noticed in free-radical additions to 1-chloro-4-*t*-butylcyclohexene (**3**) (run 26 in Table III, **16**:**17** = 1.3 for thiolacetic acid addition; run 29, **24**:**25** = 0.5 for hydrogen sulfide addition; and run 32, **23**:**33** = 0.5 for methanethiol addition in Table V).

Electrostatic repulsion or steric compression between the equatorial thiyl substituent at C-2 and the incoming transfer agent might account for the variation. Another alternative involves interaction of the equatorial thiol–acetoxy substituent with the radical center, possibly *via* a bridged intermediate such as **60**. This type of interaction is not available to thiols. Approach of the transfer agent from the bottom (axial direction) is not possible. We do not favor this type of interaction, because no significant increase in the **12**:**13** ratio is observed at high thiolacetic acid concentration or low temperatures. It may well be that other factors are involved, but these are not discernible at present.



60



61

In every case where direct comparison can be made, the ratio of axial to equatorial chain transfer is lower from intermediate **59** (X = Cl) than from the positional isomer **61**. This undoubtedly reflects the fact that, for a *t*-butylcyclohexane derivative, the 1,3-diaxial interactions of the hydrogen geminal to the *t*-butyl group are larger than those of the axial hydrogen vicinal to the *t*-butyl.

Free-radical additions of thiolacetic acid to 1- and 2-methyl-4-*t*-butylcyclohexenes (**4**, **5**) also show a preference for axial thiyl-radical attack. This preference increases from 2:1 to at least 6:1 (*cf.* runs 42 and 43 in Table VII). Reactions carried out with varying acid to olefin ratios again resulted in changes of the relative proportions of axial and equatorial thiyl-radical attack.

The differences in the stereochemistry of thiolacetic acid additions between the chloro olefins **1** and **3** and the methyl olefins **4** and **5** are striking. First of all, the concentration effect is *opposite*. Also, the amount of product with axial attachment of –SAc *increases* with increasing temperature in the methyl olefin series. Additionally, no diaxial adduct (*e.g.*, **46** or **50**) is observed with the methyl olefins, and, for the adducts with equatorial –SAc, *cis* addition producing diequatorial adduct is much more dominant with the methyl olefins **4** and **5**. These remarkable variations prompt us to propose that, for additions to the methyl-4-*t*-butylcyclohexenes, reversibility from the twist-boat radical **58**, X = CH_3 (Scheme I) is important and is inhibited by high thiolacetic acid concentrations and that chain transfer to give products with equatorial –SAc groups takes place with **58**, X = CH_3, rather than with the chair conformer **59**, X = CH_3.

As before, the kinetic addition process favors higher production of the 2-axial thiyl intermediate **57**, X = CH_3, over the twist-boat intermediate **58**, X = CH_3. However, the conformational inversion **58** ⇌ **59** no longer favors the chair form **59** when X = CH_3. There appears to be a substantial amount of bond opposition strain between the methyl group and the vicinal equatorial –SAc group in **59** (X = CH_3) that is relieved in the twist form **58**. Since the energy difference between **58** and **59**, X = CH_3, is lowered and probably favors **58**, and, since **58**, X = CH_3, is of higher energy than **57**, X = CH_3, the reverse process **58** → **5** + AcS· is facilitated. At high thiol concentration, the lifetime of **58**,

X = CH_3, is shortened and chain transfer gives greater amounts of **51** + **52**.

Although chain transfer can occur from either **58** or **59** (X = CH_3), chain transfer from the flexible form **58**, X = CH_3, is supported by the observation of an increase in the amounts of products **52** and **51** with a decrease in reaction temperature (runs 43, 44; 46, 47; 48, 49 in Table VII).

An examination of Dreiding models indicates that chain transfer from **58**, X = CH_3, *cis* to the thiol acetoxy moiety is less sterically hindered than chain transfer from the opposite direction. The transition state for equatorial chain transfer from **59**, X = CH_3, requires that the methyl group begin to assume an axial position, and, owing to the rather large conformational energy of an axial methyl substituent, the activation energy for this process will be greater than that for axial chain transfer. In any case, either **58** or **59** (X = CH_3) is predicted to give the diequatorial diastereomer **52** as the major product.

The *cis* (*e*-SAc, *a*-Cl) (**12**) product predominated in the chloro analogue. This reversal in the preferred direction of chain transfer with the two intermediates derived from equatorial thiolacetoxy-radical addition to 2-chloro- and 2-methyl-4-*t*-butylcyclohexene (**1** and **5**) lends support to the suggestion that the nature of the product-determining intermediates is different in each case.

All reference to geometry at the radical center has been purposely avoided in the above discussion. At low temperature and high concentration of chain-transfer agent, the 9-decalyl radicals appear to maintain a large degree of configurational or conformational integrity.[25,26] Esr measurements support a planar cyclohexyl radical.[27] Based on the above observations, there is no reason to assume that the radical intermediates are capable of configurational stability. Whether the intermediates are best represented by a sp^2-hybridized carbon atom or by a rapidly equilibrating sp^3 species, is for the moment a moot point. In the transition state of chain transfer, the carbon atom has undoubtedly acquired sp^3 character.

Conclusion

The previously reported[4] finding that the degree of stereoselectivity of free-radical thiol additions to 1-chlorocyclohexene depended on the thiol to olefin ratio has not been observed in studies of such additions to several other substituted cyclohexenes,[10-12] although in all cases investigated, the major products of the reactions resulted from *trans* addition. The studies described in this work have demonstrated that *trans*-diaxial addition predominates in free-radical additions of thiols to "rigid" cyclohexenes, and that the relative proportions of products are *indeed* dependent on the addendum to olefin ratio.

Unlike the stereospecific free-radical additions of hydrogen bromide to certain cyclic olefins,[3,9] the additions of thiols were only stereoselective. The decrease in stereoselectivity with thiols can best be explained in terms of the reversal of the thiyl-radical addition step. Differences in the extent of reversibility appear to be dependent upon the relative stabilities of the thiyl radicals and the 2-thiyl-1-substituted cyclohexyl radicals, and the rate of chain transfer. The concentration and temperature effects observed for free-radical additions of thiols to 1- and 2-chloro-4-*t*-butylcyclohexene (**3**, **1**) relative to those for 1- and 2-methyl-4-*t*-butylcyclohexene (**4**, **5**) are of the same order of magnitude but in opposite directions. The different conformations of the cyclohexyl-radical intermediates arising from equatorial thiyl-radical addition is thought to be responsible for the opposing trends. Free-radical additions with thiolacetic acid and hydrogen sulfide displayed the greatest degree of reversibility in the initial thiyl-radical addition step.

Experimental Section[28]

Materials.—Unless otherwise stated, reagents were obtained from commercial sources. The Dow Chemical Co., Midland, Mich., supplied a generous gift of 4-*t*-butylcyclohexanone. Thiolacetic acid was distilled twice. The center fraction of the second distillation was used for the free-radical additions. Methanethiol was passed through Drierite before it was condensed in the reaction vessel. Hydrogen sulfide was first passed through Drierite and phosphorus pentoxide before it was condensed. Benzyl mercaptan was used without further purification. Anhydrous magnesium sulfate was the drying agent.

1-Chloro-4-*t*-butylcyclohexene (3).—A procedure outlined by Mousseron and Jacquier[29] for the preparation of 1-chlorocyclohexene and recently reported by Readio and Skell[10] for the synthesis of **3** was used, bp 71.5–72° (4.3 mm) [lit.[10] bp 82.5–83° (7 mm)].

2-Chloro-4-*t*-butylcyclohexene (1).—A mixture of 20 g (0.06 mol) of 2^e-chloro-4^e-*t*-butylcyclohexyl tosylate (**2**)[30] and 300 ml of 5% potassium hydroxide in isopropyl alcohol was heated at 45–50° for 2 hr. The mixture was poured onto a mixture of ice and dilute hydrochloric acid, and the product was extracted with pentane. The extract was washed with 5% sodium bicarbonate solution and with water, and was dried and concentrated to give 11.0 g of crude vinyl halide, which was distilled to yield 8.5 g (85%) of 2-chloro-4-*t*-butylcyclohexene (**1**), bp 51–52° (1 mm), $n^{25}D$ 1.4802. The product gave only one peak on gc with a column containing 30% by weight of silicone 550 fluid on Chromosorb P at 182°.

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.55; H, 9.92; Cl, 20.53. Found: C, 70.02; H, 9.87; Cl, 20.15.

The ir spectrum of the vinyl chloride was characterized by bands at 1662 and 826 cm^{-1}.

1-Methyl-4-*t*-butylcyclohexene (4).—The method of LeBel and Ecke[13] was employed; the compound had bp 43–44° (4.5 mm) [lit. bp 60–62° (6 mm)].

2-Methyl-4-*t*-butylcyclohexanols.—A solution of 80 g (0.49 mol) of 2-methyl-4-*t*-butylphenol in 300 ml of glacial acetic acid was hydrogenated employing 6 g of platinum oxide catalyst. The solution was filtered, diluted with an equal volume of water, and continuously extracted with pentane for 12 hr. The pentane extract was washed with sodium bicarbonate solution until the

(25) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Amer. Chem. Soc.*, **87**, 2590 (1965).

(26) F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875 (1967).

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

(28) Melting points are corrected and boiling points are uncorrected. The microanalyses were by Midwest Microlabs, Inc., Indianapolis, Ind. Perkin-Elmer grating spectrophotometers, Models 237B and 621, were used for the determination of the ir spectra. Liquids were run as films between sodium chloride plates, and solids were run in carbon disulfide in 0.1-mm sodium chloride cells. A Varian Associates A-60A spectrometer was used for the nmr spectra, deuteriochloroform or carbon tetrachloride were the solvents, and tetramethylsilane was the internal standard. F and M Gas Chromatographs, Models 775 and 810, equipped with thermal conductivity cells, were used for gc. The following gc columns were employed: column A was an 8 ft × 0.25 in. o.d. aluminum tube, packed with 15% LAC-728 on 60–80 mesh Gas-Chrom S; column B was an 8 ft × 0.375 in. o.d. aluminum tube packed with the same material as column A; columns C and D were 8 ft × 0.25 in. o.d. and 8 ft × 0.375 in. o.d. aluminum tubes, respectively, both packed with 20% E-20,000 on 60–80 mesh Gas-Chrom S; column E was an 80 × 0.75 in. o.d. stainless-steel tube packed with 20% E-20,000 on 60–80 mesh Chromosorb P. Helium was the carrier gas.

(29) M. Mousseron and R. Jacquier, *Bull. Soc. Chim. Fr.*, 648 (1950).

(30) N. A. LeBel and R. F. Czaja, *J. Org. Chem.*, **26**, 4768 (1961).

washings remained basic, and then washed twice with water. The solution was dried and concentrated to give a crude yield of 74 g. Distillation yielded a volatile forerun of 9 g, bp 28–29° (0.5 mm). Continued distillation afforded 57 g (69%), bp 58–62° (0.2 mm), of the alcohols.

Dehydration of the 2-Methyl-4-*t*-butylcyclohexanols.—To a solution of 69 g (0.41 mol) of the mixture of alcohols in 150 ml of toluene contained in a flask fitted with a Barrett water trap was added 1 g of *p*-toluenesulfonic acid. The solution was heated to reflux. When, after 2 hr at reflux, no water had collected in the trap, 1 ml of concentrated sulfuric acid was added. After 24 hr, 5.3 ml (*ca.* 70% of theory) of water had been removed. The solution was cooled to room temperature, and was washed with sodium bicarbonate solution and water. The toluene was removed by distillation at reduced pressure. Further distillation gave the following fractions: (1) 32 g, bp 95° (35 mm); (2) 20 g, bp 60° (0.5 mm). Gc analysis of fraction 1 on column C at 80° showed 3 minor and 2 major products. The major products (**5**, **6**) were present in equal proportion and comprised 90% of the product mixture. Preparative gc employing column E at 100° permitted separation of 2-methyl-4-*t*-butylcyclohexene (**5**) and 1-methyl-3-*t*-butylcyclohexene (**6**). An analytical sample of **5** had bp 82–82.5° (18 mm), n^{24}D 1.4640.

Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.72; H, 13.6.

Fraction 2 was shown to be homogeneous by gc employing column C at 160°. The material solidified on standing. Recrystallization from pentane followed by sublimation (45°, 1 mm) afforded a pure sample of 2^t-methyl-4^t-*t*-butyl-cyclohexanol (**7**), mp 61–62°.

Conversion of 2-Methyl-4-*t*-butylcyclohexene (5) to a Mixture of *cis*- and *trans*-2-Methyl-4-*t*-butylcyclohexanones.—The method of Brown and Garg[31] was used for the hydroboration and oxidation of **5**. Distillation of the crude product mixture afforded 0.2 g of product, bp 60° (oil bath, 0.5 mm). Analysis by gc (column C at 150°) showed that some starting olefin contaminated the product. Elution chromatography on a 70 × 6 mm neutral alumina column using pentane as the eluent gave an 80:20 mixture of *cis*- and *trans*-2-methyl-4-*t*-butylcyclohexanones, respectively, as shown by gc and ir spectrum comparisons with an 85:15 mixture of authentic material.[15]

Catalytic Hydrogenation of the Methyl-*t*-butylcyclohexenes.—A solution of 0.152 g (0.001 mol) of 2-methyl-4-*t*-butylcyclohexene (**5**) in 5 ml of absolute ethanol was hydrogenated employing 0.020 g of 10% palladium on carbon as the catalyst. After work-up, gc analyses on column C at 80° indicated that the isomeric *cis*- and *trans*-1-methyl-3-*t*-butylcyclohexanes were formed in 86:14 proportion, respectively. 1-Methyl-3-*t*-butylcyclohexene (**6**) was reduced and analyzed in a similar manner. Two products in a ratio 84:16 were observed. Gc and ir analysis indicated that the hydrocarbon mixtures obtained from reduction of **5** and **6** were identical. Two products in the ratio 80:20 were formed on reduction of 1-methyl-4-*t*-butylcyclohexene (**4**). The two components were assumed to be *trans*- and *cis*-1-methyl-4-*t*-butylcyclohexane, respectively. The reduction products from **4** were shown to be different from those obtained from the reduction of **5** and **6** by ir and gc analysis.

2^t-Methyl-4^t-*t*-butylcyclohexyl Tosylate (7-OTs).—The alcohol **7** (12.6 g) was converted to the tosylate by way of the usual low-temperature reaction with *p*-toluenesulfonyl chloride and pyridine.[32] After work-up, there was obtained 22 g (92%) of viscous yellow oil which solidified on standing at room temperature. The tosylate was used without further purification. Recrystallization of a sample from pentane gave white needles, mp 62.0–62.5°.

***cis*-1-Methyl-3-*t*-butylcyclohexane.**—A solution of 2.0 g (0.0062 mol) of the crude tosylate (7-OTs) in 10 ml of anhydrous ether was added drowpise to a stirred suspension of 0.470 g (0.013 mol) of lithium aluminum hydride in 25 ml of anhydrous ether over a period of 0.5 hr, while the temperature was maintained at 20–25°. The mixture was refluxed for 5 hr. After the usual work-up, distillation afforded 0.61 g (65%), bp 75° (*ca.* 20 mm), of pure *cis* hydrocarbon, n^{25}D 1.4575. That this hydrocarbon was not the *trans* isomer was shown by the infrared spectrum, which did not possess a band at 620–640 cm^{-1}.[33] Gc analysis on column C at 80° showed it to have an identical retention time as the major product from the reduction of **5**.

Free-Radical Addition of Hydrogen Bromide to 2-Chloro-4-*t*-butylcyclohexene (1).—Hydrogen bromide (anhydrous) was passed through a solution containing 0.1 g (5 mol %) of benzoyl peroxide and 1.0 g (0.006 mol) of vinyl chloride **1** in 100 ml of olefin-free pentane for 2.5 hr at room temperature. The reaction mixture was further stirred for 8 hr and hydrogen bromide was again passed in for another hour. The reaction mixture was added to crushed ice, and the aqueous layer was extracted with pentane. The pentane layer was washed with sodium bicarbonate solution and water, dried, and concentrated. The crude product (1.25–1.30 g) was analyzed by gc. A sample was shown to contain 2^c-chloro-4^c-*t*-butylcyclohexyl bromide (**8**) (80%), vinyl chloride **1** (5%), and another volatile material (15%), which was not identified. The pure bromochloride (**8**) was isolated by chromatography on alumina. Recrystallization from pentane afforded a white, crystalline solid, mp 56–57°. The ir spectrum showed bands at 680 and 736 cm^{-1}, attributed to axial bromo and equatorial chloro stretching frequencies, respectively.

Anal. Calcd for $C_{10}H_{18}BrCl$: C, 47.36; H, 7.15. Found: C, 47.25; H, 7.20.

Dipole Moment Determination.—The dielectric constants were obtained using a commercial apparatus previously described.[34] The moments were calculated by essentially the method of Halverstadt and Kumler, utilizing an IBM 650 computer. Reagent grade benzene was used as the solvent. The dielectric constants and densities of various mole fractions were measured at 25°, and the value $\mu = 3.71 \pm 0.04$ D was obtained.

The Reaction of Phosphorus Tribromide with 2^t-Chloro-4^t-*t*-butylcyclohexanol (9).—The chlorohydrin **9**[30] (4 g, 0.0021 mol) was added to an ice–salt cooled mixture of 6.0 g of phosphorus tribromide and 2 ml of pentane. The bath was allowed to warm to room temperature, and after 48 hr, water was added. The aqueous layer was extracted with pentane and the extract was washed with sodium bicarbonate solution and water and was dried. The residue after concentration (4.6 g) was chromatographed on 150 mg of Merck acid-washed alumina. The column was eluted with 650 ml of pentane and 250 ml of 10% ether–pentane. Fractions of 50 ml were collected. The pentane fractions contained 1.45 g (27%) of a colorless liquid which solidified immediately, mp 56–57°. A mixture melting point with the bromide **8** did not depress. The 10% ether–pentane fractions contained 0.5 g (16%) of starting material.

Reaction of Potassium *t*-Butoxide with 2^c-Chloro-4^c-*t*-butylcyclohexyl bromide. (8).—Potassium (*ca.* 0.2 g) was dissolved in 100 ml of dry *t*-butyl alcohol. The solution was maintained at 55° and 1.0 g of **8** was added. The mixture was stirred for 45 min, water was added, and the aqueous alcohol layer was extracted several times with pentane. The pentane layers were combined, washed, and concentrated. Approximately 0.7 g of a yellow oil remained. Rapid distillation led to the isolation of 0.60 g (90%) of a clear liquid, n^{24}D 1.4790. Gc and ir comparison with an authentic sample[30] showed it to be 2-chloro-4-*t*-butylcyclohexene (**1**).

Addition of Thiolacetic Acid to 1-Chloro- and 2-Chloro-4-*t*-butylcyclohexene (3, 1). Method A. Azobisisobutyronitrile (AIBN) Initiated Addition.—A solution of 0.500 g (0.00289 mol) of chloro olefin, **1** or **3**, and 0.024 g (5 mol %) of AIBN in the appropriate olefin-free solvent was flushed with nitrogen for 15 min at room temperature. The required amount of thiolacetic acid was added with a hypodermic syringe, and the reaction vessel was lowered into an oil bath held at the desired temperature. In the cases of reactions carried out at the reflux temperature of the solution, the oil bath was 10–15° above the boiling point of the solvent. After 1 hr, the reaction solution was cooled with an ice bath and diluted with pentane. The pentane solution was washed with sodium bicarbonate solution and water, dried, concentrated, and analyzed by gc on column A at 175° with a flow rate of 180 ml/min.

For those reactions carried out in sealed tubes, the reagents were placed in Pyrex tubes; after flushing with nitrogen, the tubes were sealed and placed in a constant-temperature bath for 1 hr. The tubes were then cooled and opened. The work-up and analysis followed the above procedure.

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Method B. Ultraviolet Light Initiated Addition.—The apparatus used consisted of a 2-l. vessel wrapped with aluminum foil and fitted with a water inlet tube, a water outlet tube, a Hanau S-87 quartz immersion lamp, and a quartz reaction tube which was placed about 1 cm away from the lamp. The reaction tube was equipped with a nitrogen inlet and outlet tube. Thiolacetic acid, chloro olefin 1 or 3 (0.500 g, 0.00289 mol), and the solvent were added to the reaction tube. The tube was flushed with nitrogen for 15 min, and then was irradiated for 1 hr. The work-up described in method A was used.

In the ultraviolet light induced reactions at −60°, the water bath was replaced by a 2-propanol–Dry Ice bath. In the case of sealed tube reactions, the reagents were placed in Pyrex tubes, flushed with nitrogen, sealed, and mounted 1 cm away from the light source. The results are shown in Tables I, II, and III.

Separation of the 2-Chloro-4-*t*-butylcyclohexanethiol Acetates (10–13).—Gc analysis on column A at a flow rate of 180 ml/min at 175° showed four components with retention times of 7.5, 9.2, 10.9, and 13.4 min, respectively. Products from several free-radical additions of thiolacetic acid to 1 were combined and distilled, bp 80–82° (0.03 mm). The compounds were separated by preparative gc employing column B at 180°. The two major compounds (retention times 9.2 g and 13.4 min, respectively) were separated from the somewhat volatile liquid phase by distillation. The remaining two components were purified by chromatography over silica gel using pentane as the eluent. Reexamination by gc indicated that no decomposition or rearrangement had occurred.

The component of 7.5-min retention time was identical with 2^t-chloro-4^c-*t*-butylcyclohexexanethiol acetate (11), as shown by comparison of gc retention times and ir spectra.

The second compound (9.2 min gc retention time), 2^c-chloro-4^t-*t*-butylcyclohexanethiol acetate (12), solidified on standing and was sublimed (40°, 0.02 mm) to give a product having mp 79–80°; nmr δ 3.72 (1 H, 2 = $W_{1/2}$ = 21 Hz) and 4.50 (1 H, $W_{1/2}$ = 8 Hz); ir 675 and 740 cm^{-1}.

Anal. Calcd for $C_{12}H_{21}ClOS$: C, 57.92; H, 8.50; Cl, 14.24. Found: C, 58.22; H, 8.60; Cl, 14.35.

The structure of the compound of 10.9-min retention time, 2^t-chloro-4^t-*t*-butylcyclohexanethiol acetate (13), was assigned on the basis of its infrared and nmr spectra. The nmr had a complex multiplet at δ 3.25–3.85 (2 H); ir 725 cm^{-1}.

The component of 13.4-min retention time had an identical gc retention time and infrared spectrum as 2^c-chloro-4^c-*t*-butylcyclohexanethiol acetate (10).

***cis*-4-*t*-Butylcyclohexene Sulfide.**—Potassium thiocyanate (3.25 g, 0.033 mol) was dissolved in 4 ml of a 1:1 mixture of water and ethanol, and the solution was stirred for 30 min at room temperature. Two grams (0.013 mol) of *trans*-4-*t*-butylcyclohexene oxide[30] was added. The mixture was stirred for 36 hr, poured into water, and extracted with pentane. The pentane layers were combined, washed with water, dried, and concentrated. The crude product was rapidly distilled to yield 1.80 g (81%) of a colorless liquid, oil-bath temperature 85–90° (0.5 mm), n^{24}D 1.5087. The infrared spectrum indicated the absence of *trans*-4-*t*-butylcyclohexene oxide.

Anal. Calcd for $C_{10}H_{18}S$: C, 70.52; H, 10.65; S, 18.82. Found: C, 70.80; H, 10.71; S, 18.59.

2^t-Chloro-4^c-*t*-butylcyclohexanethiol Acetate (11).—*cis*-4-*t*-Butylcyclohexene sulfide (0.30 g, 0.0017 mol) was added to an excess of acetyl chloride (3 ml) and the mixture was stirred overnight at room temperature. The reaction mixture was added to crushed ice and extracted with pentane, and the pentane layers were combined and washed with sodium bicarbonate solution and water. After drying and concentration, a pale yellow liquid (*ca.* 0.4 g) remained, which was rapidly distilled. A colorless liquid, 0.27 g (61%), n^{24}D 1.5062, was isolated, which solidified after standing. Recrystallization from pentane afforded the thiol acetate 11: mp 50–51°; nmr δ 4.00 (1 H, $W_{1/2}$ = 8 Hz) and 4.40 (1 H, $W_{1/2}$ = 6 Hz); ir 680 cm^{-1}.

Anal. Calcd for $C_{12}H_{21}OSCl$: C, 57.92; H, 8.51; Cl, 14.25. Found: C, 58.00; H, 8.45; Cl, 14.46.

2^c-Chloro-4^c-*t*-butylcyclohexanethiol (18).—Approximately 1.2 g of the addition product resulting from the ultraviolet light catalyzed addition of hydrogen sulfide to 2-chloro-4-*t*-butylcyclohexene (1) was added to 25 ml of 70% aqueous ethanol. The reaction mixture was heated for 45 min and water was added. The aqueous ethanol layer was extracted with pentane and the pentane layers were combined, washed several times with water, dried, and concentrated. The crude product was rapidly distilled and *ca.* 1.0 g of 18, oil-bath temperature 100–110° (0.3–0.5 mm), n^{25}D 1.5078, was obtained.

Anal. Calcd for $C_{10}H_{19}SCl$: C, 58.09; H, 9.26; Cl, 17.15. Found: C, 58.24; H, 9.36; Cl, 17.26.

2^c-Chloro-4^c-*t*-butylcyclohexanethiol Acetate (10).—Acetic anhydride (2 ml) was added to 0.250 g of 2^c-chloro-4^c-*t*-butylcyclohexanethiol (18) in 6 ml of anhydrous pyridine. The mixture was refluxed for 20 min and then was added to a mixture of dilute hydrochloric acid and crushed ice. The aqueous layer was extracted several times with pentane. The pentane layers were combined, washed with sodium bicarbonate solution and water, dried, and concentrated. The crude product was rapidly distilled [oil-bath temperature, 135–140° (0.2–0.3 mm)], and 0.25 g was collected, n^{25}D 1.5078. 2^c-Chloro-4^c-*t*-butylcyclohexanethiol acetate (10) was shown to give only one peak on gc, column A at 175°; nmr complex multiplet at δ 3.78–4.58 (2 H); ir 735 and 710 cm^{-1}.

Anal. Calcd for $C_{12}H_{21}SOCl$: C, 57.92; H, 8.51; S, 12.88. Found: C, 58.27; H, 8.51; S, 13.20.

Saponification and Reacetylation of the 2-Chloro-4-*t*-butylcyclohexanethiol Acetates (10–13).—A solution of 1.0 g (0.004 mol) of the thiolacetate adducts 10–13 in 10 ml of ethanol was flushed with nitrogen for 10 min. An equivalent amount of sodium ethoxide in ethanol was added. After the solution had been stirred at 50° for 1 hr, the reaction mixture was poured into cold water, acidified to pH 1 with dilute hydrochloric acid, and extracted with ether. The extracts were washed with water, dried, and concentrated. The crude product was treated with 2 ml of acetic anhydride and 1 drop of pyridine. This mixture was heated to reflux for 15 min, cooled, and poured into cold water. After extraction with ether and the usual work-up, analysis by gc on column A at 175° showed 10 and 12 as the only chlorothiolacetate products.

Saponification and Subsequent Methylation of the 2-Chloro-4-*t*-butylcyclohexanethiol Acetates (10–13).—A solution of 0.483 g (0.0194 mol) of the thiolacetate adducts (10–13) in the proportion 53:8:26:14 (10:11:12:13) in 5 ml of ethanol was cooled to 0° and flushed with nitrogen for 10 min. An equivalent amount of sodium ethoxide in ethanol was added, and the solution was stirred at 0° for 10 min. An excess of methyl iodide (2 ml) was added and the mixture was stirred at 0° for 1 hr, and was allowed to stand at room temperature for 5 hr. The mixture was poured into ice and water, and was extracted with ether. The ether extract was washed twice with water, dried, and concentrated. Gc analysis of the product mixture on column A at 140° showed two chloro methyl sulfides 26 and 28 in a 68:32 proportion. The *cis*-thiol acetates 10 and 12 were present in the ratio of 67:33 in the original thiol acetate mixture.

Addition of Hydrogen Sulfide to 1-Chloro- and 2-Chloro-4-*t*-butylcyclohexene (3, 1).—The apparatus described in method B of the addition of thiolacetic acid to vinyl chlorides 3 and 1 was used. In addition, the reaction tube was equipped with a Dry Ice condenser. The olefin (3 or 1) (1.0 g, 0.00578 mol) was added; the tube was cooled to −80°; and 1.5–2 ml of hydrogen sulfide was condensed. In the case of addition to 1, 6 ml of olefin-free hexane was added. The cooling bath was removed and after a short period was replaced with a water bath. The refluxing solution was irradiated for 1 hr, after which time the hydrogen sulfide was allowed to vaporize. The crude chlorothiols 18–21 and 22–25 were quantitatively acetylated at 0° with acetic anhydride and pyridine as the catalyst. Analysis was performed by gc at 175° on column A, and the data is summarized in Tables IV and V.

Addition of Methanethiol to 1-Chloro- and 2-Chloro-4-*t*-butylcyclohexene. Method A. AIBN-Initiated Addition.—Methanethiol (*ca.* 1 ml) was condensed in a Pyrex tube at 0°. The tube was warmed to room temperature to remove some of the thiol, stoppered, cooled, and weighed. This process was repeated until 0.070 g (0.00145 mol) of methanethiol remained. After cooling, 0.012 g of AIBN (5 mol %), 0.250 g (0.00145 mol) of 1, and 2.9 ml of hexane were added. The tube was sealed and placed in an oil bath at 86° for 1 hr, cooled, and opened. The mixture was concentrated and placed under vacuum at room temperature for 2 hr. Analysis was by nmr.

Method B. Ultraviolet Light Initiation.—The apparatus described for the additions of hydrogen sulfide was used for the additions of methanethiol to 3. The chloro olefin 3 (4.93 g, 0.0287 mol) and 5 ml of methanethiol were added, and the mixture was irradiated for 2 hr. Hexane (6 ml) was used as the solvent for the reaction carried out at −60°. The reaction mixture was

concentrated, and crystallization from pentane at −20° usually afforded about 3 g of the major *cis* adduct **30**. Recrystallization yielded 2 g of pure 2^{c}-chloro-5^{t}-*t*-butylcyclohexyl methyl sulfide (**30**). The mother liquors were combined, concentrated, and analyzed by nmr. Preparative gc afforded a pure sample of 2^{c}-chloro-5^{c}-*t*-butylcyclohexyl methyl sulfide (**32**). The nmr spectra of **30** and **32** agreed with those published.[10]

The procedure of method A, except that AIBN was omitted, was used to prepare hexane solutions of 0.250 g (0.00145 mol) of **1** and the required amount of methanethiol in sealed tubes. The solutions were irradiated at 5° for 1 hr. After removing and concentrating the samples, the relative proportions of adducts were obtained by nmr and are listed in Table IV.

Synthesis of the Diaxial Chlorocyclohexyl Alkyl and Aryl Sulfides (27, 31, 35, 39).—A slight excess of the appropriate thiol was added to a solution of sodium ethoxide in ethanol. After stirring for 15 min, an equivalent amount of the required 4-*t*-butylcyclohexene oxide[30] was added. The mixture was heated under reflux for 3 hr and was then stirred at room temperature overnight. The mixture was then poured into cold water and acidified with dilute acetic acid, and the product was extracted with ether. The ether extract was washed with sodium bicarbonate solution and water, dried, and concentrated to give the diaxial hydroxy sulfide.

The hydroxy sulfide was converted to the corresponding chlorides using thionyl chloride in a mixture of benzene and pyridine at 0°. After the mixture had been stirred overnight at room temperature, it was poured onto crushed ice and extracted with pentane. The extract was washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and water. The solution was dried and concentrated. Distillation afforded about a 70% yield (based on epoxide) of the desired diaxial chlorosulfides.

2^{t}-Chloro-5^{t}-*t*-butylcyclohexyl methyl sulfide (31) had bp 75° (oil bath, 0.07 mm), n^{24}D 1.5048.

Anal. Calcd for $C_{11}H_{21}ClS$: C, 59.83; H, 9.58; Cl, 16.05. Found: C, 60.10; H, 9.39; Cl, 15.87.

2^{t}-Chloro-4^{c}-*t*-butylcyclohexyl methyl sulfide (27) had bp 65° (oil bath, 0.07 mm), n^{24}D 1.5045.

Anal. Calcd for $C_{11}H_{21}ClS$: C, 59.83; H, 9.58; Cl, 16.05. Found: C, 60.06; H, 9.68; Cl, 15.70.

2^{t}-Chloro-4^{c}-*t*-butylcyclohexyl benzyl sulfide (35) and 2^{t}-Chloro-5^{t}-*t*-butylcyclohexyl benzyl sulfide could not be distilled without significant amounts of rearrangement. The nmr and ir were consistent with the assumed diaxial structures.

2^{t}-Chloro-4^{c}-*t*-butylcyclohexyl phenyl sulfide (39) had bp 140–145° (oil bath, 1.0 mm), n^{24}D 1.5531.

Anal. Calcd for $C_{16}H_{23}SCl$: C, 67.93; H, 8.18; Cl, 12.53. Found: C, 68.09; H, 8.21; Cl, 12.33.

Addition of Benzyl Mercaptan to 2-Chloro-4-*t*-butylcyclohexene. Method A. AIBN-Initiated Addition.—The procedure employed was essentially that used for the additions of thiolacetic acid to **1**. The olefin **1** (0.250 g, 0.00145 mol), 0.170 ml (0.00145 mol) of benzyl mercaptan, 2.8 ml of hexane, and 0.012 g (5 mol %) of AIBN were placed in a Pyrex tube and flushed with nitrogen. After sealing, the tube was placed in an oil bath at 86° for 1 hr. The tube was cooled in an ice–water bath and opened. The sample was concentrated by removing all volatiles *in vacuo*. Relative proportions of the benzyl sulfides were determined by nmr analysis.

Method B. Ultraviolet Light Initiated Addition.—The quantities used were identical with those used in method A, except that AIBN was omitted. The solution was irradiated in a sealed tube at 5° for 1 hr, and after concentration, the proportions of products were determined by nmr analysis. The results are summarized in Table IV.

Saponification and Subsequent Reaction with Benzyl Iodide of the 2-Chloro-4-*t*-butylcyclohexanethiol Acetates (10–13).—The procedure used for the preparation of a mixture of the two methyl sulfides **26** and **28** from the chlorothiol acetates **10–13** was employed. Benzyl iodide was used as the alkylating agent. After work-up the excess benzyl iodide was removed by distillation at 30–35° *in vacuo*. The two singlets for the benzyl protons of the *cis* compounds were separated by 10.6 Hz in the nmr spectrum; δ 3.82 for the benzyl proton resonance of **34** and δ 3.64 for the benzyl proton band of **36**.

Free-Radical Addition of Thiophenol to 2-Chloro-4-*t*-butylcyclohexene (1). Method A. Benzoyl Peroxide Initiated Addition.—Thiophenol (5.1 g, 0.047 mol) was added to a mixture of 0.28 g of benzoyl peroxide (5 mol %) and 4 g (0.023 mol) of vinyl halide **1** (2:1 molar ratio). The flask was evacuated several times to remove oxygen and then the reaction was allowed to proceed at 60° for 1 week. Water was added and the mixture was extracted with pentane. The extract was washed several times with cold sodium bicarbonate solution and water, dried, and concentrated. A yellow oil (6 g) remained. Distillation under reduced pressure gave 1.95 g (49%) of starting olefin. Further distillation yielded 2.35 g (30–35%), n^{24}D 1.5704, of adduct contaminated with *ca.* 10% diphenyl disulfide. Molecular distillation afforded 0.5 g of pure adduct, n^{24}D 1.5588, which was divided into two portions and analyzed.

A typical analysis was conducted in the following manner. A weighed portion of the adduct was heated to reflux in 80% ethanol for 2 hr. Upon cooling and acidification with nitric acid, the chloride concentration (4–5%) was determined by the Volhard method.

Method B. Ultraviolet Light Initiated Addition.—The apparatus described for the additions of thiolacetic acid was used. Thiophenol (6.60 g, 0.006 mol) was added to 5.15 g (0.003 mol) of **1** (2:1 molar ratio) in a Vycor tube, and this mixture was degassed at 10^{-3}–10^{-4} mm. The tube was sealed, placed in the reaction tube, and irradiated for 48 hr, after which time excess thiophenol and olefin were distilled from the adduct.

The mixture was taken up in pentane and then was washed several times with cold aqueous hydroxide solution to remove thiophenol. The pentane layer was washed with dilute hydrochloric acid, sodium bicarbonate solution, and water, dried, and concentrated. Distillation afforded 2.5 g (55%) of **1** and 3.5 g of adduct which was contaminated with diphenyl disulfide. Upon standing, the diphenyl disulfide precipitated, and redistillation gave 3.0 g (35%) of adduct.

After solvolysis of the adduct mixture in 75% aqueous ethanol for 1 hr, Volhard analysis indicated 6–7% of titrable chloride. The organic material was recovered by extracting the mixture with carbon tetrachloride. The extracts were combined, dried, and concentrated. The residue (*ca.* 2.5 g) was placed on a chromatography column consisting of 50 g of Merck acid-washed alumina, and 40-ml fractions were taken. It required 400 ml of pentane to remove 2^{c}-chloro-4^{c}-*t*-butylcyclohexyl phenyl sulfide (**38**). The column was then washed with anhydrous ether and 0.20 g of a highly viscous residue was collected. An infrared spectrum of the crude residue showed bands at 3300 and 960 cm^{-1} (axial OH).

A quantitative infrared comparison showed that this product consisted of approximately 73% 2^{t}-phenylsulfo-4^{c}-*t*-butylcyclohexanol (**43**) and 27% 2^{t}-phenylsulfo-5^{t}-*t*-butylcyclohexanol. The mixture was treated with *p*-nitrobenzoyl chloride, and a crystalline derivative was obtained which corresponded to the *p*-nitrobenzoate of **43**, mp 99–101°, mmp 99–101°. A mixture melting point with the *p*-nitrobenzoate of 2^{t}-phenylsulfo-5^{t}-*t*-butylcyclohexanol (mp 100–101°) was 86–91°.

2^{t}-Chloro-4^{t}-*t*-butylcyclohexyl Phenyl Sulfide (41).—Lithium thiophenolate (3.0 g) was added to a solution of 8.0 g (0.022 mol) of **2**[30] in 300 ml of dry THF. The heterogeneous reaction mixture was heated at 65° for a period of 3 days. After filtration through Hyflo Supercel and concentration at reduced pressure, 6.6 g of crude material remained. Pentane was added and 1 g of starting material precipitated. Distillation of the mother liquors led to the isolation of 0.8 g (20%) of 2-chloro-4-*t*-butylcyclohexene (**1**). The residue from this distillation was sublimed and *ca.* 1 g of diphenyl disulfide was collected. The residue was distilled [oil-bath temperature 120° (0.05–0.10 mm)]. A pale yellow liquid, 2.7 g (40%), n^{21}D 1.5600, was isolated.

Anal. Calcd for $C_{16}H_{23}SCl$: C, 67.93; H, 8.18; Cl, 12.53. Found: C, 67.75; H, 7.99; Cl, 12.26.

Slight contamination with 2^{t}-phenylsulfo-4^{c}-*t*-butylcyclohexyl chloride—the isomer from diaxial–diequatorial rearrangement—was noted in the nmr spectrum.

Attempted chromatography of the reaction mixture led to solvolysis of the sulfide. The product from the solvolysis was tentatively assigned as 2^{t}-phenylsulfo-4^{c}-*t*-butylcyclohexanol (**43**). The infrared spectrum showed bands at 3330 and 950 cm^{-1}.

2^{c}-Chloro-4^{c}-*t*-butylcyclohexyl Phenyl Sulfide (38).—Lithium thiophenolate (7.2 g) was added to a solution of 8 g (0.0021 mol) of 2^{t}-chloro-4^{t}-*t*-butylcyclohexyl tosylate (**44**) in 200 ml of dry THF. The heterogeneous reaction mixture was heated at 60° for a period of 4 weeks and was then worked up in the usual manner. The residue was chromatographed on 120 g of Merck acid-washed alumina. The column was initially eluted with 540 ml of pentane and then with anhydrous ether. Fractions of 10 ml were

taken for the first 20 fractions, after which 25-ml fractions were taken. Fractions 1–14 yielded diphenyl disulfide. Fractions 15–31 afforded 1.10 g of yellow oil. The ether fractions gave 5.6 g (70%) of starting material. The yellow oil was chromatographed a second time, and 1.05 g (16%) of **38** was collected, $n^{25}D$ 1.5562.

Anal. Calcd for $C_{16}H_{23}SCl$: C, 67.93; H, 8.18; Cl, 12.53. Found: C, 68.15; H, 8.20; Cl, 12.70.

Reaction of 2^t-Phenylsulfo-4^c-*t*-butylcyclohexanol (43) with Raney Nickel.—Raney nickel W-2 (*ca.* 5 g) was heated with 0.5 g (0.002 mol) of the hydroxyphenylsulfide **43** in 40 ml of 95% ethanol for a period of 2 days. The reaction mixture was then filtered and concentrated. A white solid remained, 0.22 g (75%), mp 76–81°. Chromatography of a portion of this compound through a column of Merck acid-washed alumina using 5% ether–pentane as eluent gave an alcohol, mp 81–82.5°. A mixture melting point determination with an authentic sample of *cis*-4-*t*-butylcyclohexanol did not depress. The infrared spectra of an authentic sample and the product were superimposable.

2^t-Phenylsulfo-4^c-*t*-butylcyclohexyl *p*-Nitrobenzoate.—*p*-Nitrobenzoyl chloride (0.15 g) was added to approximately 0.2 g of **43** dissolved in 2 ml of anhydrous pyridine. During a period of 36 hr, the reaction mixture was warmed several times on a steam bath. The mixture was then added to crushed ice, acidified with dilute hydrochloric acid, and extracted several times with ether. The ether layer was washed with dilute acid, sodium bicarbonate solution, and water, dried, and concentrated. A yellow oil remained and trituration with pentane led to the isolation of yellow crystals. Recrystallization from a mixture of 1 drop of ethyl acetate in pentane afforded pale yellow crystals, mp 102–103°.

Anal. Calcd for $C_{23}H_{27}SNO_4$: C, 66.80; H, 6.58; S, 7.75. Found: C, 67.01; H, 6.78; S, 7.52.

2^t-Phenylsulfo-5^t-*t*-butylcyclohexyl *p*-Nitrobenzoate.—The *p*-nitrobenzoate was synthesized from the hydroxy sulfide in the usual manner. Recrystallization from pentane gave yellow crystals, mp 101–102°. A mixture melting point with the *p*-nitrobenzoate of **43** was depressed.

Anal. Calcd for $C_{23}H_{27}SNO_4$: C, 66.80; H, 6.58; S, 7.75. Found: C, 67.01; H, 6.78; S, 7.52.

Desulfurization of 2^t-Phenylsulfo-5^t-*t*-butylcyclohexanol.—Employing the procedure described earlier, 0.75 g of hydroxy sulfide was desulfurized, and 0.11 g (25%) of *trans*-3-*t*-butylcyclohexanol was recovered. The compound was sublimed, mp 64.5–66°. A mixture melting point with an authentic sample did not depress, and the ir spectra were superimposable.

Free-Radical Addition of Thiolacetic Acid to 1-Methyl- and 2-Methyl-4-*t*-butylcyclohexene (4, 5). Method A. AIBN-Initiated Addition.—A hexane solution of 0.220 g (0.00145 mol) of olefin (**4** or **5**), 0.012 g (5 mol %) of AIBN, and the required amount of thiolacetic acid were placed in a Pyrex tube and flushed with nitrogen. The tube was sealed and placed in an oil bath at 86° for 1 hr. Excess thiolacetic acid was removed by washing with sodium bicarbonate solution, followed by washing with water, drying, and concentrating. The relative proportions of products were determined by gc using column C at 160°.

Method B. Ultraviolet Light Initiated Addition.—The procedure was similar to that of method A except that AIBN was omitted and the addition was initiated by means of uv light using the apparatus described for the additions of thiolacetic acid to the chloro olefins 1 and **3**. The results of thiolacetic acid additions to **4** and **5** are shown in Table VI and VII.

Analysis and Separation of the 2-Methyl-4-*t*-butylcyclohexanethiol Acetates (49, 51, 52).—Gc analysis using column C at 160° with a helium flow rate of 180 ml/min showed three thiolacetates, **49**, **51**, and **52**, with retention times of 17.9, 20.0, and 22.0 min, respectively. An analytical sample was prepared by combining the products from three reactions followed by distillation: bp 72° (0.08 mm).

Anal. Calcd for $C_{13}H_{24}OS$: C, 68.36; H, 10.59. Found: C, 68.33; H, 10.68.

The two adducts which were produced in the greatest proportion, **49** and **52**, were separated by preparative gc employing column D at 170°. The diequatorial adduct **50** was the component with a retention time of 17.9 min on column A, and diastereomer **49** had a retention time of 20.0 min under the same conditions.

2^c-Methyl-4^c-*t*-butylcyclohexanethiol Acetate (49).—To a solution of 13 g (0.04 mol) of 2^t-methyl-4^t-*t*-butylcyclohexyl tosylate (**7**-OTs) in 50 ml of DMF was added 5 g (0.089 mol) of sodium hydrosulfide under an atmosphere of nitrogen. The reaction mixture was stirred at 60° for 2 days. The mixture was poured into ice and water, and was acidified to congo red with dilute hydrochloric acid. The product was extracted with pentane, and the extract was washed with water, dried, and concentrated. Distillation afforded 5 g (67%) of 2^c-methyl-4^c-*t*-butylcyclohexanethiol (**49**-SH), bp 47° (0.2 mm).

The thiol (1 g, 0.0054 mol) was acetylated using 3 ml of acetic anhydride and two drops of pyridine. After stirring at room temperature for 24 hr, the reaction mixture was poured into cold water and extracted with pentane. The extract was washed with sodium bicarbonate solution and water, dried, and concentrated. Distillation yielded 0.950 g (78%) of thiolacetate **49**, bp 79° (0.08 mm), $n^{25}D$ 1.4912.

Desulfurization of the 2-Methyl-4-*t*-butylcyclohexanethiol Acetates.—A mixture of 0.40 g (0.0018 mol) of thiol acetate adducts **49**, **52**, and **51** in the proportion 79:18:3, respectively, was heated under reflux in 15 ml of ethanol in the presence of 2.5 g of Raney nickel (W-2) for 1.5 hr. After filtration, the ethanol solution was diluted with water and the product was extracted with pentane. The extract was washed with water, dried, and concentrated to give 0.2 g (74%) of product, which was analyzed by gc using column C at 80°. The ratio of *cis*- to *trans*-1-methyl-3-*t*-butylcyclohexane was 90:10.

2-Methyl-4-*t*-butylcyclohexanethiols (49-SH, 53, 54).—To a solution of 0.52 g (0.0023 mol) of the thiol acetates **49**, **52**, and **51** in the proportion 73:21:6, respectively, in 3 ml of ethanol was added a solution of 0.0025 mol of sodium ethoxide in 5 ml of ethanol. After the mixture had been stirred at room temperature for 1 hr, it was diluted with water and acidified to congo red with 10% hydrochloric acid. The aqueous solution was extracted with pentane, and the extract was washed with water, dried, and concentrated. Distillation gave 0.30 g (71%) of product, bp 49° (0.2 mm). Gc analysis did not give good resolution of the thiols. However, reacetylation with acetic anhydride and pyridine gave the same thiol acetates **49**, **52**, and **51** in an identical proportion as that noted for the starting material.

Desulfurization of the 2-Methyl-4-*t*-butylcyclohexanethiols.—A mixture of 0.16 g (0.0007 mol) of thiols obtained from the corresponding thiol acetates in the previous experiment was desulfurized with 1.5 g of Raney nickel (W-2) in 5 ml of ethanol. The ethanol solution was diluted with water, dried, and concentrated. The proportion of *cis*- and *trans*-1-methyl-3-*t*-butylcyclohexane was 91:9, as determined by gc analysis.

Registry No.—**1**, 17002-25-4; **5**, 15822-50-1; **8**, 20708-94-5; **10**, 20708-95-6; **11**, 20708-96-7; **12**, 20708-97-8; *cis*-4-*t*-butylcyclohexene sulfide, 20708-98-9; **18**, 20708-99-0; **27**, 20709-00-6; **31**, 20709-01-7; **38**, 20709-02-8; **39**, 20728-48-7; **41**, 20728-49-8; **43** (*p*-nitrobenzoate), 20709-03-9; 2^t-phenylsulfo-5^t-*t*-butylcyclohexyl *p*-nitrobenzoate, 20728-50-1; **49**, 20709-04-0; **49**-(SH), 20728-51-2.

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