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STEREOCHEMICAL ASPECTS OF THE FREE RADICAL ADDITION OF METHANETHIOL TO 4-t-BUTYLCYCLOHEXENE

E. S. HUYSER and J. R. JEFFREY[1]
Department of Chemistry, The University of Kansas, Lawrence, Kansas

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Abstract—The photochemically-induced additions of methanethiol to 4-t-butylcyclohexene yielded a mixture of the four isomeric sulphides, *cis* and *trans* 4-t-butylcyclohexylmethyl sulphides and *cis* and *trans* 3-t-butylcyclohexylmethyl sulphides. The less stable axially substituted isomers, *cis* 4-t-butylcyclohexylmethyl sulphide and *trans* 3-t-butylcyclohexymethyl sulphide, were formed in amounts five to seven times greater than the equatorially substituted isomers. The stereochemical control observed in this free radical addition reaction is proposed to be the result of the conformational factors encountered in the addition of the methanethiyl radical to the double bond of 4-t-butylcyclohexene. The role of the reversibility of the addition of thiyl radicals to 4-t-butylcyclohexene is discussed in terms of the stereospecificity noted in these addition reactions.

THE free radical additions of thiols and thioacids to 1-substituted cycloalkenes have been reported to yield mainly a *cis* addition product resulting from the *trans* addition of the thiol or thioacid to the double bond.[2] Stereospecific *cis* additions were reported by Cristol and Arganbright to occur in the addition of *p*-thiocresol to 1-chlorobicycloalkenes.[3] It is quite likely that the steric factors exerted by the substituent bonded to the double bond as well as other groups in the immediate vicinity of the double bond as in the case of the bicycloalkenes may influence the stereochemistry of these addition reactions to a significant extent. The work described here, namely the addition of methanethiol to 4-t-butylcyclohexene, is concerned with the stereochemical control exerted by a substituent positioned far enough from the double bond to exclude any direct steric influence on the addition reaction.

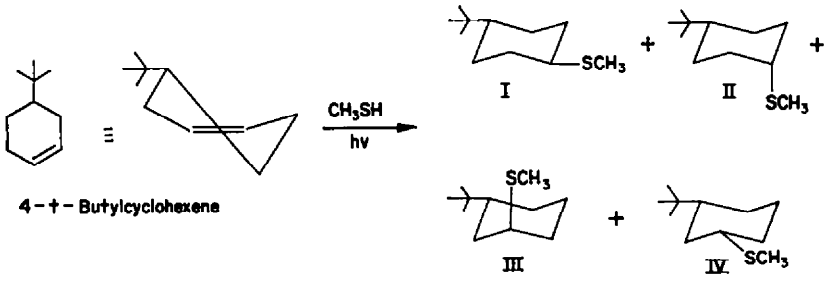
RESULTS

The photochemically-induced addition of methanethiol to 4-t-butylcyclohexene yielded the four expected thioethers, *trans* 4-t-butylcyclohexylmethyl sulphide (I), *cis* 4-t-butylcyclohexylmethyl sulphide (II), *trans* 3-t-butylcyclohexylmethyl sulphide (III) and *cis* 3-t-butylcyclohexylmethyl sulphide (IV), as addition products. The addition products were identified by comparison of their gas chromatographic retention times on three different columns with those of authentic samples of the isomeric sulphides (Table 1). In each case, the addition of a portion of the authentic

[1] National Science Foundation Fellow, 1963–1964. The work described was taken from the thesis submitted by J. R. J. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas (1964).

[2] H. L. Goering, D. I. Relyea and D. W. Larsen, *J. Amer. Chem. Soc.* **78**, 348 (1956); H. L. Goering, D. I. Relyea and K. L. Howe, *Ibid.* **79**, 2502 (1957); F. G. Bordwell and W. A. Hewett, *Ibid.* **79**, 3493 (1957); H. Behringer and W. Kley, *Liebigs Ann.* **595**, 160 (1955).

[3] S. J. Cristol and R. P. Arganbright, *J. Amer. Chem. Soc.* **79**, 6039 (1957).



sample increased the peak area of only that peak assigned to the isomer in the gas chromatograms of the reaction mixtures.

The authentic samples of the axially substituted sulphides (II and III) were prepared by direct displacement of the equatorial *p*-toluenesulphonate groups from *trans* 4-t-butylcyclohexyl-*p*-toluenesulphonate and *cis* 3-t-butylcyclohexyl-*p*-toluenesulphonate respectively by reaction of these tosylates in methanol with potassium methyl sulphide. Similar treatment of *cis* 4-t-butylcyclohexyl-*p*-toluenesulphonate

TABLE 1. GAS CHROMATOGRAPHIC RETENTION TIMES OF THE SULPHIDES

	Retention times (min)		
	Column[a] A	Column[a] B	Column[a] C
First peak in reaction mixture	16·9	31·1	8·5
Authentic sample of III	16·9	31·0	8·4
Second peak in reaction mixture	18·5	33·1	9·2
Authentic sample of II	18·4	32·9	9·0
Third peak in reaction mixture	20·3	34·7	10·5
Authentic sample of IV	20·5	34·4	10·3
Fourth peak in reaction mixture	24·1	41·1	12·6
Authentic sample of I	24·0	41·1	12·5

[a] Gas chromatographic columns are described in the Experimental section.

and *trans* 3-t-butylcyclohexyl-*p*-toluenesulphonate resulted in extensive amounts of elimination yielding t-butylcyclohexenes,[4] rendering this approach to the equatorially substituted isomers (I and IV) impractical. Synthesis of mixtures, containing I and II in one case from which I was isolated by preparative gas chromatography and III and IV in another case from which IV was similarly isolated, were accomplished in the following manner: Reaction of 4-t-butylcyclohexanone with hydrogen sulphide and hydrogen chloride yielded 4-t-butylcyclohexanethione which was reduced immediately[5] with LAH to a mixture of *cis* and *trans* 4-t-butylcyclohexanethiols. Treatment of this mixture with sodium ethoxide in ethanol followed by methyl iodide yielded a mixture of I and II which was separated into the pure components by preparative gas chromatography. The authentic sample of IV was obtained from the same series of reactions starting with 3-t-butylcyclohexanone.

[4] S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.* 77, 5562 (1955).

[5] Both 3- and 4-t-butylcyclohexanethiones were evil-smelling red oils which on standing were converted to colourless trimers.

Confirmation of the assignment of structure of the four isomeric sulphides came from the reactions of their sulphones in ethanolic sodium ethoxide. Sulphones having this functionality in an axial position have been reported to epimerize in basic medium to the isomeric sulphone having the functionality in an equatorial position.[6] Thus, the sulphone of II, the axially substituted isomer, was epimerized to that of I when heated with sodium ethoxide in ethanol whereas the sulphone of I underwent no

TABLE 2. COMPOSITION OF THE ADDITION PRODUCT MIXTURES

Thiol:Olefin	Temp (°C.)	I	II	III	IV
1·52	0	6·7	49·3	37·6	6·3
1·37	0	4·7	51·0	38·6	5·6
0·61	0	6·7	50·9	37·6	4·6
0·53	0	6·5	50·4	37·1	6·0
0·42	0	7·1	49·4	36·3	7·1
0·24	0	6·3	50·0	36·3	7·5
0·13	0	7·1	50·9	35·5	6·4
7·37	19·5	5·7	48	39·6	6·7
6·21	19·5	5·2	47·7	41·1	6·0
5·65	19·5	4·3	48·7	41·1	5·8
3·70	19·5	5·1	47·9	41·9	5·2
3·03	19·5	5·5	48·3	40·1	6·0
2·22	19·5	6·1	48·7	39·7	5·5
0·93	19·5	5·0	49·9	38·6	5·6
0·75	19·5	5·1	48·1	39·1	7·7
0·60	19·5	6·6	50·3	37·2	5·9
0·18	19·5	8·2	49·2	35·8	6·7
0·12	19·5	8·1	50·7	36·1	6·3
2·45	40·0	6·6	48·9	37·1	7·4
1·19	40·0	6·6	47·9	35·5	8·0
1·02	40·0	5·9	50·0	38·1	5·9
0·74	40·0	7·5	47·9	38·9	5·7
0·66	40·0	6·1	51·4	34·3	8·1
0·50	40·0	6·6	50·8	35·3	7·2
0·22	40·0	8·2	49·4	32·8	9·4

change when subjected to the same treatment. Similarly, the sulphone of the axially substituted sulphide (III) was epimerized to the sulphone of IV when heated with sodium ethoxide in ethanol whereas the latter sulphone underwent no change under these conditions.

Quantitative determination of the amounts of the four isomers formed in the photochemically-induced additions of methanethiol to 4-t-butylcyclohexene were obtained from the integrated peak areas of the four isomers making appropriate corrections for the differences in the mole ratios with respect to the area ratios by using correction factors obtained from chromatograms of known mixtures of the authentic sulphides. Table 2 shows the results of reactions performed at different temperatures and at various initial thiol:olefin ratios. The temperature of the reaction in the range of 0° to 40° had little effect on the distribution of the isomers. The only perceptible change noted was a small increase in the amount of III with a small (and evenly distributed) concurrent decrease in the amounts of the other isomers as the ratio of methanethiol to 4-t-butylcyclohexene was increased.

[6] E. L. Eliel and B. P. Thill, *Chem. & Ind.* 88 (1963).

DISCUSSION

The results in Table 2 show that II and III, the two less stable isomers with the thiomethyl group in an axial position, are formed in greater amounts than I and IV, the more stable isomers with the thiomethyl group in an equatorial position, suggesting that the stereospecificity is a matter of kinetic control in the addition reaction rather than thermodynamic equilibrium of the products. The addition reaction, under the conditions used in our experiments, proceeds by a free radical chain sequence involving addition of a methanethiyl ($CH_3S\cdot$) to the double bond giving an adduct radical which abstracts a hydrogen atom from the methanethiol. The stereochemistry is determined in the reaction of the methanethiyl radical with the double bond rather than in the hydrogen abstraction reaction since it is immaterial whether the elements of thiol add *cis* or *trans* to the double bond in these additions. The methanethiyl radical can approach both the 1- and 2-carbons of the double bond without any direct steric influence of the t-butyl group. The approach from the side *cis* to the t-butyl group yields the *cis* isomers (II and IV) whereas the approach *trans* to the t-butyl group yields the *trans* isomers (I and III). Our results show that attack by the methanethiyl radical at the 2-carbon is preferred when the approach is *trans* to the t-butyl group and attack at the 1-carbon is preferred when the approach is *cis* to the t-butyl group. The observed preferences may be due to the conformational changes that occur in the ring system when the methanethiyl radical bonds with a planar sp^2 hybridized carbon of the double bond converting it to a pyramidal sp^3 hybridized carbon. Attack from the *trans* side at the 1-carbon yields the adduct radical A· which has a twist-boat conformation whereas attack from the same side at the 2-carbon gives radical B· which has a chair conformation. When the attack is from the *cis* side at the 1-carbon, the adduct radical C·, which has a chair conformation, is formed and attack at the 2-carbon from the *cis* side yields D·, a radical with a twist-boat conformation. The twist-boat conformer of cyclohexane has been estimated to be less stable than the chair conformer to the extent of about 5·5 kcal/mole.[7] Consequently, the adduct radicals A· and D· with the twist-boat conformation might be expected to be less stable and therefore formed at slower rates than those having the more stable chair conformation.[8] Hydrogen abstraction from the methanethiol by the adduct radicals C· and B· yields the axially substituted isomers II and III respectively. The adduct radicals A· and D· may either abstract hydrogen from the methanethiol yielding the twist-boat conformers of I and IV respectively or the adduct radicals may isomerize to the chair conformers E· and F· before hydrogen abstraction (see later discussion).

A factor that may also play a role in directing the methanethiyl radical to the 2-carbon when the attack is *trans* and to the 1-carbon when the attack is *cis* is the primary steric effect exerted by the psuedo-axial hydrogens on the 3- and 6-carbons of the 4-t-butylcyclohexene. The *trans* approach at the 1-carbon and the *cis* approach

[7] W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frish, L. H. Dreyer and W. N. Hubbard, *J. Amer. Chem. Soc.* **82**, 1255 (1960); **83**, 606 (1961).

[8] The slower rate of formation of radicals with twist-boat conformations with respect to those with chair conformations has been proposed independently by F. Bordwell, P. S. Landis and G. S. Whitney to account for the predominant formation of *trans* 3- and *cis* 4-t-butylcyclohexyl thioacetates observed in the addition of thioacetic acid to 4-t-butylcyclohexene. F. Bordwell, private communication.

at the 2-carbon by the methanethiyl radical may be hindered to some extent by the psuedo-axial hydrogens on the 6- and 3-carbons respectively.[9]

Our reason for performing the reactions over a range of methanethiol: olefin ratios was to determine if the reversibility of the thiyl radical additions to alkenes[10] influenced the distribution of the products. If this were an important factor, changing the methanethiol concentration would alter the distribution of the products. The amounts of products obtained from the less stable adduct radicals which would undergo elimination more readily should be expected to increase relative to the others as the methanethiol concentration is increased provided the initially formed adduct radicals are involved in hydrogen abstraction from the methanethiol. Our results show that there is no increase in the amounts of I and IV relative to II and III over a large range of methanethiol concentrations. A plausible explanation for the lack of a concentration effect is that the twist-boat adduct radicals A· and D· isomerize to the chair conformers E· and F· faster than they can undergo elimination of the methanethiyl radical or react with the methanethiol yielding the twist-boat conformers of I and IV. Elimination of the methanethiyl radical from E· and F· can occur only if they isomerized back to the less stable twist-boat radicals A· and D· (principle of microscopic reversibility), a reaction that would be slow compared to hydrogen abstraction even if the methanethiol were present in a low concentration.

It is interesting to note that the expected concentration effect is observed as far as the relative amounts of II and III are concerned[11] if it is assumed that the somewhat lower percentage of III formed relative to II reflects the somewhat lower stability of C· relative to B·. In this case, the radicals involved in the hydrogen abstraction from the methanethiol are also those involved in the reversible addition of the methanethiyl radical.

EXPERIMENTAL[12]

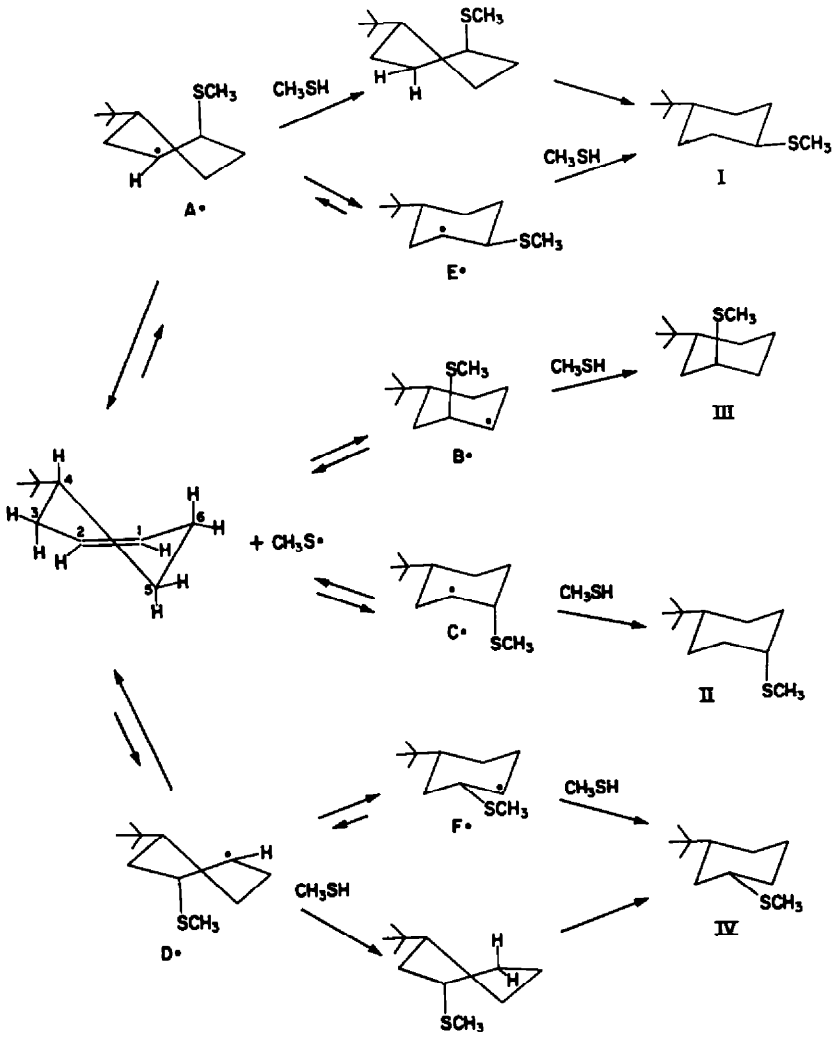
Materials and equipment. 4-t-Butylcyclohexene (b.p. 170–171°, n_D^{20} 1·4567) was prepared by pyrolysis at 400–425° of a mixture of *cis* and *trans* 4-t-butylcyclohexyl acetates obtained from acetylation of a mixture of *cis* and *trans* 4-t-butylcyclohexanols (Dow Chemical Co.). Fractional distillation of the mixture of the acetates through a 24 in. Podbielniak column yielded a pure sample of *trans* 4-t-butylcyclohexyl acetate which on hydrolysis gave *trans* 4-t-butylcyclohexanol (m.p. 81–82°, reported, 81–82° [4]). 4-t-Butylcyclohexanone was supplied by the Dow Chemical Co. A mixture of *cis* and *trans* 3-t-butylcyclohexanols was prepared by hydrogenation of 3-t-butylphenol (Aldrich Chemical Co.) over Raney nickel at 1250 psig. Gas chromatographic analysis showed the mixture obtained consisted of 85% *cis* 3-t-butylcyclohexanol and 15% of the *trans* isomer. 3-t-Butylcyclohexanone (b.p. 89–92° at 8 mm, n_D^{20} 1·4605) was prepared in 81% yield by chromic acid oxidation of 3-t-butylcyclohexanol. Methanethiol (Matheson Co.) was passed through anhydrous $CaSO_4$, condensed at −80°, and redistilled into the reaction vessels. All other reagents and solvents were commercial and were purified, when necessary by standard procedures.

[9] Although the stereospecificity observed could be explained in terms of the conformational and steric factors outlined for reactions of bridged thiyl radicals, there is no evidence for the existence of such species. Indeed, the *cis*-additions of thiols to 1-substituted bicycloalkenes tend to exclude bridged thiyl radicals from serious consideration as a necessary feature for stereospecific thiol additions *via* a free radical mechanism.[3]

[10] C. Walling and W. Helmreich, *J. Amer. Chem. Soc.* **81**, 1144 (1959).

[11] A least squares treatment of the data collected at the three temperatures showed in each case an increase in the percentage of III with a decrease in the percentage of the other isomers as the concentration of methanethiol increased.

[12] All m.ps and b.ps are uncorrected. Elemental analyses were performed by Weiler and Strauss, Oxford, England.



The gas chromatographic analyses were performed on an Aerograph Model Hy-Fl (Wilkens Corp.) equipped with a hydrogen flame detector. An Aerograph Model A-700 Autoprep was used for the gas chromatographic separations. The qualitative studies were performed on these two instruments and on an Aerograph Model A-90-P. Column A was a 10 ft. by $\frac{3}{8}$ in. Cu-tube packed with 30% diethylene glycol succinate on Chromosorb W. Column B was a 24 ft. by $\frac{1}{4}$ in. Cu-tube consisting of a 10 ft. section packed with 20% diethylene glycol succinate on Chromosorb W, a 10 ft. section packed with 20% phenyldiethanolamine succinate on Chromosorb W followed by a 4 ft. section packed the diethylene glycol succinate packing. Column C was a 5 ft. by $\frac{1}{4}$ in. Cu-tube packed with 10% lead laurate on Chromosorb P.

Photo-induced reactions of methanethiol with 4-t-butylcyclohexene. The results in Tables 1 and 2 were obtained from reactions performed using the following general procedure: About 0·33 g (0·0024 mole) of 4-t-butylcyclohexene was accurately weighed into a previously weighed Pyrex tube. After flushing with dry N_2 and cooling in a Dry Ice-Cellosolve bath, methanethiol was condensed in the tube. The tube was sealed and the amount of methanethiol added determined by weighing the two parts resulting from the sealing operation. The sealed tube was placed in a constant temp water bath and illuminated with a 275 watt General Electric Sunlamp. The reactions were generally complete after 30 min of illumination. After cooling to $-80°$, the tube was opened and any unreacted

methanethiol allowed to evaporate slowly. The resulting reaction mixture was subjected to gas chromatographic analysis. The quantitative determinations were made on Column B in the Aerograph Model Hy-Fl whereas the retention time studies were made on all three columns described above.

cis 4-*t-Butylcyclohexylmethyl sulphide* (II). *trans* 4-t-Butyl cyclohexyl-*p*-toluenesulphonate (m.p. 89–90°; reported, 89·4–90°)[4] was prepared in 82% yield by reaction of *trans* 4-t-butylcyclohexanol with *p*-toluenesulphonyl chloride in pyridine. A portion of this material (18·0 g, 0·06 mole) was allowed to react at room temp for 48 hr in 100 ml of anhydrous MeOH with 75 ml of a 1·0 molar solution of potassium methyl sulphide prepared by reaction of K with methanethiol in MeOH. The resulting reaction mixture was poured into a mixture of ice and HCl aq and extracted 3 times with 50 ml portions of ether. The combined ether extracts were washed 3 times with water and dried over $MgSO_4$. Removal of the ether yielded an oil which on distillation gave 8·0 g (73% of theory) of crude *cis* 4-t-butylcyclohexylmethyl sulphide. After purification by preparative gas chromatography on Column A, the material was redistilled; b.p. 99–100° at 7·5 mm, n_D^{20} 1·4912. (Found: C, 70·57; H, 11·63. Calc. for $C_{11}H_{22}S$: C, 70·89; H, 11·90%.) Oxidation of a portion of the sulphide with H_2O_2 yielded the sulphone of *cis* 4-t-butylcyclohexylmethyl sulphide; m.p. 171·5–172·5°; reported, 176·5–177·5°.[6] (Found: C, 60·68; H, 10·08. Calc. for $C_{11}H_{22}SO_2$: C, 60·51; H, 10·16%.) Heating a portion of the sulphone at 100° in EtOH containing a 10% excess EtONa yielded a sulphone, m.p. 134–135° which showed no depression in m.p. when mixed with the sulphone obtained from *trans* 4-t-butylcyclohexylmethyl sulphide.

trans 3-*t-Butylcyclohexylmethyl sulphide* (III). A mixture consisting of 85% *cis* 3-t-butylcyclohexanol and 15% of the *trans* isomer was converted to a mixture of the corresponding *p*-toluenesulphonates by reaction with *p*-toluenesulphonyl chloride in pyridine. The crude *p*-toluenesulphonate mixture was recrystallized once from an ethyl acetate–pet. ether (b.p. 30–60°) mixture and dried. A small portion was recrystallized to a constant m.p. of 58·5–59·5° which agrees with that reported (58·0–59·5°)[4] for *cis* 3-t-butylcyclohexyl-*p*-toluenesulphonate. A portion of the crude *p*-toluenesulphonate (6·2 g, 0·02 mole), and 25 ml of 1·0 molar potassium methyl sulphide were mixed and stirred for 48 hr at room temp. The reaction mixture was worked up in the manner described in the previous experiment and yielded a mixture amounting to 2·80 g (75% of theory) consisting of 95% *trans* 3-t-butylcyclohexylmethyl sulphide, 4% *cis* 3-t-butylcyclohexylmethyl sulphide and 1% of a mixture of 3- and 4-t-butylcyclohexenes. A sample of pure *trans* 3-t-butylcyclohexylmethyl sulphide was obtained by preparative gas chromatographic separation of the mixture on Column A; b.p. 97–98° at 7·5 mm, n_D^{20} 1·4880. (Found: C, 70·58; H, 11·79. $C_{11}H_{22}S$ requires: C, 70·89; H, 11·90%.) Oxidation of a portion of this material yielded the *sulphone of* trans 3-*t-butylcyclohexylmethyl sulphide*, m.p. 87–88·5°. (Found: C, 60·38; H, 10·06. $C_{11}H_{22}SO_2$ requires: C, 60·51; H, 10·16%.) Heating the sulphone at 100° overnight in EtOH containing 10% EtONa converted the sulphone to one melting at 109–110·5°. This m.p. was not depressed when the material was mixed with the sulphone of *cis* 3-t-butylcyclohexylmethyl sulphide which melted at the same temp.

trans 4-t-*Butylcyclohexylmethyl sulphide* (I). 4-*t*-Butylcyclohexanone (200 g, 1·31 mole) was dissolved in 400 ml abs EtOH. Over a period of 2 hr, H_2S and HCl gases were bubbled into the stirred solution which was cooled with an ice bath. Ice water (200 ml) was added to the resulting red solution. The 4-t-butylcyclohexanethione was extracted from the resulting mixture with three 200 ml portions of ether. The ether extracts were combined, washed once with 100 ml of 10% $NaHCO_3$ aq, 3 times with 100 ml portions of water (until the washings were neutral) and then dried with 50 g anhydrous $MgSO_4$. The drying period was kept below 10 min because of the rapid trimerization of the thione. The ether solution of the thione was filtered slowly through a fritted glass disc into a slurry of LAH (19·0 g, 0·5 mole, 50% excess based on 4-t-butylcyclohexanone) in 200 ml of ether. After stirring for 1 hr, the reaction mixture was decomposed with water and dil. HCl. The ether layer was washed, dried over anhydrous $MgSO_4$ and, after evaporation of the ether, yielded a crude mixture of *cis* and *trans* 4-t-butylcyclohexanethiols (160 g. 72% of theory) most of which (155 g, 0·90 mole) was dissolved in 400 ml of abs. EtOH. One mole (23 g) of clean Na was added to the solution. After all of the sodium had reacted, 129 g (0·91 mole) of MeI was added dropwise at such a rate to maintain a reaction temp of 30°. The solution was allowed to stand overnight at room temp and was then poured with stirring into a solution of 200 ml conc. HCl aq in 500 ml water. The resulting mixture was extracted 3 times with 150 ml portions of ether, the extracts were combined, washed and dried over anhydrous $MgSO_4$. Removal of the ether yielded 164 g (96% of theory based on thiol) of a mixture

of *cis* and *trans* 4-t-butylcyclohexylmethyl sulphides (b.p. 99–104° at 7·5 mm). The highest boiling fraction resulting from fractionation on a 24 in. Podbielniak column contained 90% of the *trans* isomer and 10% of the *cis* isomer, the retention time of which was identical with the material prepared by the displacement reaction described above. Samples of both the *cis* and *trans* 4-t-butylcyclohexylmethyl sulphides were obtained by preparative gas chromatographic separation of a portion of the mixture. Reaction of a portion of the *trans* 4-t-butylcyclohexylmethyl sulphide (b.p. 103–104° at 7·5 mm, n_D^{20} 1·4885. (Found: C, 70·65; H, 11·71. Calc. for $C_{11}H_{22}S$: C, 70·89; H, 11·90%) with H_2O_2 yielded the sulphone (m.p. 135·5–136·5, reported, 136–137°.[6] (Found: C, 60·11; H, 9·98. Calc. for $C_{11}H_{22}SO_2$: C, 60·51; H, 10·16%) which could be recovered unchanged after heating at 100° overnight in EtOH containing a 10% excess EtONa.

cis 3-*t-Butylcyclohexylmethyl sulphide* (*IV*). 3-t-Butylcyclohexanone (23·0 g, 0·15 mole) was dissolved in 150 ml abs. EtOH. The solution was stirred while H_2S and HCl gases were bubbled into the solution over a period of 90 min. Ice water (150 ml) and ether (100 ml) were added to the resulting reaction mixture. The water phase was separated and extracted twice with 100 ml portions of ether. The combined ether extracts were added to the ether layer, washed with water, then with a 10% $NaHCO_3$ aq and finally with water again and dried for 10 min over anhydrous $MgSO_4$. The resulting red solution of 3-t-butylcyclohexanethione was filtered off the $MgSO_4$ and added dropwise into a slurry of LAH (2·0 g, 40% excess based on 3-t-butylcyclohexanone) in 100 ml of anhydrous ether. After stirring for 1 hr, 10 ml of ethyl acetate were added to destroy the excess LAH and the mixture was poured into 100 g of 10% H_2SO_4 aq and ice. The aqueous phase was extracted twice with 100 ml portions of ether. The ether layer and the extracts were combined and washed with water until neutral and dried over anhydrous $MgSO_4$. Evaporation of the ether left 22·0 g of an orange coloured oil which on distillation yielded 20·4 g (79% of theory based on the starting ketone) of a mixture of *cis* and *trans* 3-t-butylcyclohexanethiols (b.p. 94–100° at 10 mm). The mixture of thiols (17·2 g, 0·10 mole) was dissolved in EtOH and 2·5 g (0·11 mole) of clean Na was added with stirring. After all of the Na had reacted, 14·5 (0·11 mole) of MeI was added dropwise and the reaction mixture stirred overnight. Workup of the resulting mixture in the manner describe in the previous experiment yielded 17·5 g (94% of theory based on the thiol mixture) of a crude mixture consisting of 70% *cis* 3-t-butylcyclohexylmethyl sulphide and 30% of the *trans* isomer. Gas chromatographic separation of a portion of this mixture on Column A afforded a pure sample of *cis* 3-t-butylcyclohexylmethyl sulphide; b.p. 101–102° at 7·5 mm, n_D^{20} 1·4914. (Found: C, 70·75; H, 11·78. $C_{11}H_{22}S$ requires: C, 70·89; H, 11·90%.) The sulphone of this material melted at 110–110·5°. (Found: C, 60·85; H, 9·93. $C_{11}H_{22}SO_2$ requires: C, 60·51; H, 10·16%.) After heating overnight in EtOH containing a 10% excess EtONa at 100°, this sulphone was recovered unchanged.