Stereoelectronic Effects in Hydrogen-atom Transfer Reactions of Substituted Cyclohexyl Radicals

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Thermolysis of the peroxyoxalates (1)—(7) and the diacyl peroxides (8)—(11) in cyclohexane at 100 °C gives cycloalkenes and cycloalkanes by hydrogen-atom transfer reactions of the initially formed conformationally biased 4-t-butyl-, 4-t-butyl-*cis,cis*-2,6-dimethyl-, 4-t-butyl-*cis,trans*-2,6-dimethyl-, 4-t-butyl-*cis*-2-methyl-, 4-t-butyl-*trans*-2-methyl-, and 5-t-butyl-*cis*-2-methylcyclohexyl radicals (12)—(17). The composition of the product mixtures indicates that transfer of axial β-hydrogen atoms occurs more rapidly than does transfer of equatorial β-hydrogen atoms. These results support the hypothesis that homolytic fission of a C–H bond is favoured when it lies close to the plane of an adjacent semi-occupied orbital.

In a previous communication [1] we presented evidence that disproportionation of substituted cyclohexyl radicals, like homolytic fission of C_β–C, C_β–O, and other βγ-bonds in suitable carbon-centred radicals, is influenced by stereoelectronic factors, in that it proceeds most readily when the C–H bond undergoing fission can assume coplanarity with the adjacent semi-occupied orbital.[2,3] Similar conclusions were reached by Agosta and Wolff [4] and by Greenlee *et al.*[5] who found that the course of hydrogen-atom transfer in various photochemically generated biradicals can be rationalised on stereoelectronic grounds. A contrary result was reported by Livant and Lawler [6] who studied the disproportionation of cyclohexyl radicals by the CIDNP technique and obtained evidence for the selective fission of those C_β–H bonds (equatorial) which lie furthest from the plane of the semi-occupied orbital. We now give further examples of stereoelectronic effects on disproportionation of substituted cyclohexyl radicals together with full details of our earlier work.

Extensive e.s.r. studies [7–9] have indicated that the cyclohexyl radical at ordinary temperatures undergoes rapid interconversion between two chair-like conformers in each of which the β-protons are stereochemically non-equivalent.[7,8] The two axial C_β–H bonds lie close to the axis of the semi-occupied orbital (θ 22°) whereas the two equatorial C_β–H bonds are almost orthogonol to it (θ 82°)].[8] For most substituted cyclohexyl radicals the two possible chair-like conformations will differ in free energy and will not be equally populated. For example, the e.s.r. spectrum of the 4-t-butyl-1-hydroxycyclohexyl radical shows the presence of only one conformer.[10] As is the case for cyclohexanes the t-butyl substituent strongly favours that conformer in which it occupies an equatorial position. It is reasonable to assume, therefore, that the t-butyl groups in the radicals (12)—(17) studied in the present work will provide a strong conformational bias and will effectively ensure that each radical is conformationally homogeneous under our experimental conditions. Consequently, any difference in reactivity towards abstraction between the equatorial and axial β-hydrogen atoms in, for example, the radical (15) will be reflected in the distribution of products.

The radicals (12)—(17) were generated by thermolysis in dilute cyclohexane solution of the appropriate monoperoxyoxalates [11] (1)—(7) and, in some cases, of the diacyl peroxides (8)—(11). Product mixtures were analysed by g.l.c. and individual components were identified, after separation by chromatography on silver nitrate-impregnated silica gel, by comparison with authentic compounds.

Results and Discussion

The yields of cyclohexanes and cyclohexenes formed when the peroxides (1)—(11) were heated in dilute cyclohexane solution (0.25M) at 100 °C for 2 h are given in the Table. Since the peroxides were too unstable to be handled safely in pure form they were prepared *in situ* and the yields of products are based on the amounts of acid chlorides used for their synthesis. The total yield given in the Table for each peroxide is the highest obtained from at least two experiments. Although there was considerable variation in total yield the agreement between the relative yields of products determined in duplicate or triplicate experiments with each substrate was satisfactory (s.d. ±20%). Cyclohexene was detected in most reaction mixtures but the yields (generally >0.6 mol per mol of peroxyoxalate or >0.2 mol per mol of diacyl peroxide) were not accurately determined. Products of higher g.l.c. retention time, presumably esters and dimers, were also formed but were not unambiguously identified or determined. However, the fact that monomeric products were formed in good yield (generally 70—90%) indicates that radical coupling is not an important reaction pathway.

The results given in the Table show that each peroxide affords the appropriate substituted cyclohexane in >50% yield. Such products must arise, at least in part, by hydrogen-atom abstraction from solvent or some other donor. Although the present results do not allow the extent of this type of reaction to be estimated, the formation of cyclohexene, particularly in reactions involving diacyl peroxides, verifies that cyclohexyl radicals are generated from solvent and are involved in hydrogen-atom transfer processes.

The substituted cyclohexenes (24)—(31) formed by thermolysis of the peroxides (1)—(11) must arise by hydrogen-atom transfer from the appropriate substituted cyclohexyl radicals, either by disproportionation or by reaction with cyclohexyl radicals. Hydrogen-atom transfer to t-butoxyl radicals, although possible in experiments involving peroxyoxalates, is improbable since their rapid reaction with solvent will ensure that their stationary concentration remains very low. The fact that the diacyl peroxides (8)—(11) give product distributions very similar to those from their corresponding peroxyoxalates lends support to this view and provides evidence that reactions of both types of precursor proceed through the same radical intermediates. Also it indicates that decarboxylation of the substituted cyclohexyloxycarbonyl radicals formed initially from peroxyoxalates, although

Products from heating of peroxyoxalates and diacyl peroxides in cyclohexane at 100 °C

Peroxide	Radical	Cycloalkane	Relative yield (%)	Cycloalkene	Relative yield (%)	Total yield (%)
(1)	(12)	(18)	83	(24)	17	84
(8)	(12)	(18)	78	(24)	22	71
(2)	(13)	(20)	76	(27)	24	91
(4)	(15)	(22) *	82	(27)	1.9	88
				(29)	16.0	
(3)	(14)	(21)	81	(25)	8.3	85
				(28)	11.2	
(5)	(14)	(21)	81	(25)	9.0	83
				(28)	10.2	
(9)	(14)	(21)	80	(25)	9.5	74
				(28)	10.8	
(10)	(14)	(21)	79	(25)	9.2	71
				(28)	11.3	
(6)	(16)	(23)	81	(25)	2.9	88
				(30)	16.0	
(11)	(16)	(23)	77	(25)	4.4	68
				(30)	19.0	
(7)	(17)	(19)	83	(26)	4.5	78
				(31)	12.9	

* The product mixture also contained *ca.* 1% of the cycloalkane (20) formed from the isomeric impurity in the peroxide (4)

expected to be relatively slow,[12] is still sufficiently rapid to compete effectively with other possible processes. In summary, it appears that the major course of these thermolyses is consistent with the Scheme.

$$(RCO_2)_2 \longrightarrow 2\,R\cdot + 2\,CO_2$$

$$ROCOCO_2OBu^t \longrightarrow ROCO\cdot + CO_2 + \cdot OBu^t$$

$$ROCO\cdot \longrightarrow R\cdot + CO_2$$

$$C_6H_{12} + \cdot OBu^t \longrightarrow C_6H_{11}\cdot + Bu^tOH$$

$$C_6H_{12} + R\cdot \longrightarrow C_6H_{11}\cdot + RH$$

$$2\,R\cdot \longrightarrow R(-H) + RH$$

$$R\cdot + C_6H_{11}\cdot \longrightarrow R(-H) + C_6H_{12}\ (\text{or } RH + C_6H_{10})$$

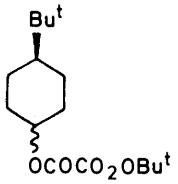
$$2\,C_6H_{11}\cdot \longrightarrow C_6H_{10} + C_6H_{12}$$

Scheme. R = Substituted cyclohexyl radical

The relative yields of cyclohexenes formed by thermolysis of the peroxides (1)—(11) indicates that there is preferential loss of axial β-hydrogen atoms from the appropriate intermediate cyclohexyl radicals. The most clear-cut demonstration of this phenomenon is provided by thermolysis of the peroxyoxalate (4). The substituted cyclohexyl radical (15) so generated has two non-equivalent β-hydrogen atoms. Abstraction of the equatorial hydrogen should be less sterically hindered and is thermodynamically favoured since it relieves non-bonded interactions of the axial methyl substituent. Nevertheless, the results show that the preferred process is the loss of the axial β-hydrogen to give the *trans*-substituted cyclohexene (29). The approximate relative values of the rate constants for β-hydrogen atom abstraction are given by the ratio of yields of the cyclohexenes (29) and (27), *i.e.* k(axial-H)/k(equatorial-H) ≈ 8.

The results of reactions involving the disubstituted radicals (14) and (16) can be similarly rationalised on the assumption that axial C_β–H bonds are more reactive than their equatorial counterparts towards hydrogen-atom transfer. Disproportionation of the radical (14) which has one axial hydrogen on each β-carbon affords approximately equal amounts of the olefins (25) and (28), whereas disproportionation of the radical (16) in which the sole axial β-hydrogen is bonded to C-6 gives a large preponderance of that olefin (30) formed by reaction at C-6. While neither of these results taken individually provides unambiguous support for the concept of enhanced reactivity for axial C_β–H bonds a comparative consideration of the data certainly points in this direction. Since each contains one tertiary and two secondary β-hydrogen atoms the statistical factor is the same for disproportionation of both of the radicals (14) and (16). Nor can the difference in the ratios of cyclohexenes, (28) : (25) and (30) : (25), formed respectively from the radicals (14) and (16) be attributed to steric or thermodynamic factors. Steric interactions should disfavour abstraction of axial β-hydrogen atoms from either radical (14) or (16) but particularly from the latter because of the proximity of the reaction centre to the axial methyl substituent. Also, fission of the tertiary C_β–H bond in (16) should be favoured thermodynamically since it relieves nonbonded interactions of the axial methyl group. Thus, both steric and thermodynamic considerations suggest that the ratio of the yield of olefin formed by homolysis of the tertiary C_β–H bond to that formed by cleavage of a secondary C_β–H bond should be greater for (16) than for (14). However, the opposite was observed. We conclude that disproportionation of the radicals involves preferentially the loss of axial β-hydrogen atoms. It is noteworthy that the radical (17) which has its sole axial β-hydrogen atom at the 6-position affords mainly the olefin (31) formed by hydrogen abstraction from C-6.

A number of experiments were conducted with the aim of confirming that the observed products do indeed arise by hydrogen atom transfer reactions of substituted cyclohexyl radicals. Thus, solvolysis of the tosylate (32h) afforded the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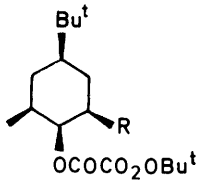
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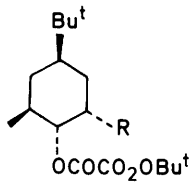
(3) R = H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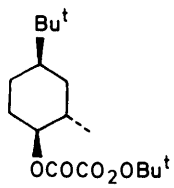
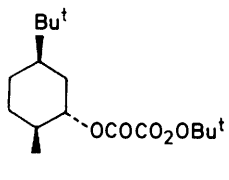

(6)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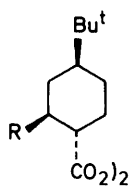
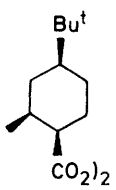

(8) R = H
(9) R = Me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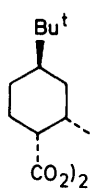
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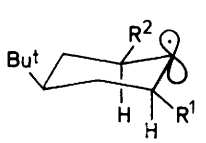
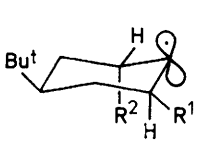
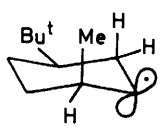

(12) $R^1 = R^2 = H$
(13) $R^1 = R^2 = Me$
(14) $R^1 = Me, R^2 = H$


(15) $R^1 = R^2 = Me$
(16) $R^1 = H, R^2 = Me$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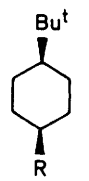
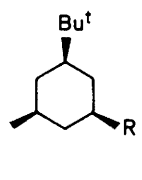
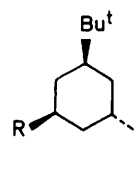
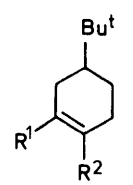
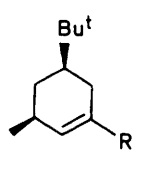
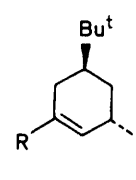

(18) R = H
(19) R = Me

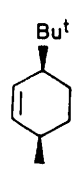

(20) R = Me
(21) R = H


(22) R = Me
(23) R = H


(24) $R^1 = R^2 = H$
(25) $R^1 = Me, R^2 = H$
(26) $R^1 = H, R^2 = Me$


(27) R = Me
(28) R = H

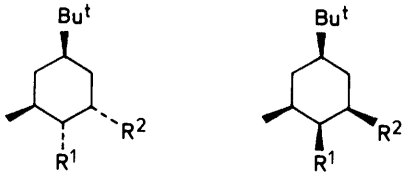

(29) R = Me
(30) R = H


(31)

cis-disubsubstituted cyclohexene (27) and rearranged olefins but none of the *trans*-compound (29), whereas decomposition of the peroxide (4) gives mainly the *trans*-disubstituted cyclohexene (29) and no rearranged products. Nor were rearranged products detected from reactions of the peroxides (1)—(11) although ionic transformations of cyclohexyl derivatives often involve rearrangement.[13] We conclude, therefore, that cationic intermediates do not play a part in the thermal decomposition of either the peroxyoxalates (1)—(7) or the diacyl peroxides (8)—(11). Likewise, both the acetate (32g) and the chloroglyoxalate of the alcohol (32d) were found to be stable to the conditions employed for thermolysis of the peroxyoxalates (1)—(7). It appears unlikely, therefore, that peroxyoxalates will undergo formation of olefins by concerted elimination of carbon dioxide and t-butyl alcohol. Finally it is noteworthy that there is very close agreement between the results of the four experiments in which the radical (14) was generated from precursors of different types and stereochemistry. This provides compelling evidence that the radical (14) is a discrete intermediate common to each of these four reactions and that the peroxide functionality is not directly involved in product formation.

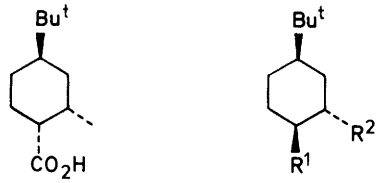
In summary, the results presented above clearly show that β-hydrogen atoms in appropriately substituted cyclohexyl radicals are chemically non-equivalent with respect to transfer processes. The most obvious interpretation is that which we have adumbrated above and has been advanced previously,[4,5] namely, that axial C_β–H bonds in chair conformations of cyclohexyl radicals undergo fission more readily than their equatorial counterparts (in our experiments some four to eight times). However, it is also possible that the apparent loss of equatorial hydrogen atoms actually involves fission of pseudo-axial C_β–H bonds in twist-boat conformations. If this were true the real preference for axial β-hydrogen atom abstraction may be greater than indicated. In any event our results suggest that it is those bonds which more effectively overlap with the adjacent semi-occupied orbital that undergo preferential fission. They are fully consistent with the view that radical disproportionation is influenced by stereoelectronic factors and conforms to a general pattern, namely, homolytic fission is most favoured when the bond concerned can assume coplanarity with an adjacent semi-occupied orbital.[2,3]

Synthesis of Radical Precursors and Reference Compounds.—The peroxyoxalates (1)—(7) were prepared by a standard procedure [11] from the appropriate alcohols *via* their chloroglyoxalates, ROCOCOCl, while the diacyl peroxides (8)—(11) were obtained by interaction of the appropriate acid chlorides with sodium peroxide.[14] *trans*-4-t-Butylcyclohexanecarboxylic acid [15] was prepared from 4-t-butylcyclohexanol *via* the bromide,[16] while the acids (32a), (33a), and (34) required for the synthesis of diacyl peroxides were obtained from 4-t-butyl-2-methylcyclohexanone [17] *via* the cyanohydrin.[18] However, attempts to obtain the acids (32b) and (33b) or their epimers at C-1 by this method failed as did a number of other



(32) (33)

a ; R^1 = CO_2H , R^2 = H
b ; R^1 = CO_2H , R^2 = Me
c ; R^1 = OH , R^2 = H
d ; R^1 = OH , R^2 = Me
e ; R^1 = OAc , R^2 = H
f ; R^1 = OTos , R^2 = H
g ; R^1 = OAc , R^2 = Me
h ; R^1 = OTos , R^2 = Me



(34) (35)

a ; R^1 = OH , R^2 = Me
b ; R^1 = Me , R^2 = OH
c ; R^1 = OTos , R^2 = Me
d ; R^1 = Me , R^2 = OAc

attempts based on nucleophilic attack on appropriate substrates. The rigidity and steric hindrance associated with such pseudo-neopentyl systems are known [19] to leave them prone to hydride shifts, alkyl rearrangements, and elimination processes in preference to nucleophilic substitution.

The alcohols (33c) and (32c) required for synthesis of the peroxyoxalates (3) and (5) were prepared by hydrogenation of 4-t-butyl-2-methylphenol,[20] while the alcohols (35a and b) were obtained by treatment of a mixture of the stereoisomers of 4-t-butylcyclohexene oxide with dimethylmagnesium.[21,22]

Although other 2,4,6-trisubstituted phenols have been hydrogenated in the presence of platinum oxide [23] this method failed when applied to 4-t-butyl-2,6-dimethylphenol. Hydrogenation over Raney nickel [24] was also unsuccessful as was attempted Birch reduction.[25] Eventually, the alcohol (33d) was obtained by treatment of the phenol in ethanol at 100 °C with hydrogen at 2 500 lb in^{-2} over 5% rhodium on alumina. At lower temperatures and pressures no hydrogenation occurred, whilst at higher temperatures the catalyst was deactivated. The alcohol (33d) was the only isomer formed. Its stereochemistry was assigned on the basis of its ^{13}C and ^1H n.m.r. spectra. Oxidation of the alcohol (33d) gave a single ketone the structure of which was assigned as *c*-4-t-butyl-*r*-2,*c*-6-dimethylcyclohexanone by n.m.r. spectroscopy. Its failure to undergo acid equilibration to a stereoisomer under the reaction conditions is surprising.[26] This ketone was epimerised at C-6 *via* its semicarbazone [27] to give *c*-4-t-butyl-*r*-2,*t*-6-dimethylcyclohexanone, which underwent highly stereoselective reduction with lithium aluminium hydride to afford the alcohol (33d).

Authentic samples of cycloalkenes required for comparison with free radical reaction products were made by appropriate elimination reactions. The trisubstituted cyclohexene (27), for example, was obtained by treatment of the alcohol (33d) with thionyl chloride in pyridine,[28] by flash pyrolysis [20] of the acetate (33g) and by interaction of the tosylate (33h) with potassium t-butoxide.[29] The same olefin (27) was the major component of the mixture formed by treatment of the alcohol (32d) with thionyl chloride or by base promoted elimination of the tosylate (32h). However, pyrolysis of the acetate (32g) proceeded, as expected,[30] mainly by *cis*-elimination to give the olefin (29).

Mixtures of the olefins (25) and (28) were obtained by similar methods from mixtures of the alcohols (32c) and (33c) or their appropriate derivatives. Interestingly, pyrolysis of the acetates (32e) and (33e) gave more of the olefin (25) than can reasonably be accounted for by a *cis*-elimination mechanism. Presumably, under vigorous conditions *trans*-elimination can occur from distorted chair conformations of the acetates (32e) and (33e). More direct evidence for this is the formation of the cyclohexene (27) from the pyrolysis of the acetate (32g). Similarly, base treatment of a mixture of the tosylates (32f) and (33f) gave more of the olefin (25) than expected on the basis of a *trans*-elimination process. It has been suggested previously [29,31] that *cis*-eliminations may occur in these systems *via* boat conformations. This is observed more directly in the formation of the cyclohexene (27) from the tosylate (32h). Pure samples of the olefins (25) and (28) were obtained from product mixtures by chromatography on silver nitrate-impregnated silica gel. A pure sample of the olefin (30) was similarly separated from the mixture with the olefin (25) obtained by base treatment of the tosylate (35c). As expected, flash vacuum pyrolysis of the acetate (35d) gave a mixture of the olefins (26) and (31) which could be separated chromatographically.

Each of the cycloalkanes (19), (21), and (23) required for comparison with free-radical reaction products was prepared by catalytic hydrogenation of the respective cycloalkenes (31), (28), and (30). Similar treatment of the olefin (27) gave a mixture of the cycloalkanes (20) and (22) in which the former predominated. Catalytic hydrogenation of a mixture of the olefins (27) and (29) gave only the cycloalkanes (20) and (22).

The assignment of stereochemistry to many of the compounds described above rests heavily on the correlation of observed ^{13}C n.m.r. shifts with those predicted by the use of addivity factors and the data already available for a variety of substituted cyclohexenes and cyclohexanes in their chair conformations.[32] Both observed and predicted values are given in the Experimental section.

Experimental

I.r. spectra for liquid films, unless otherwise stated, were recorded on either a Jasco IRA-1 or Unicam SP200 spectrometer. Mass spectra were measured on an AEI MS30 or a Hitachi–Perkin-Elmer RMU-6D instrument operating at 70 eV. ^1H N.m.r. spectra were recorded, in carbon tetrachloride unless otherwise stated, on either a Varian T60 or a JEOL JNM-PMX 60 spectrometer. ^{13}C N.m.r. spectra were recorded for solutions in deuteriochloroform on a Bruker WP-80 Fourier transform spectrometer. ^{13}C Chemical shifts were measured relative to tetramethylsilane; assignments and predicted values of chemical shifts are given in parentheses Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

G.l.c. was conducted on a Perkin-Elmer 881 or 990 instrument using the following columns; A, 0.75% FFAP on Chromosorb W (100—120), 6.0 m × 3.0 mm stainless steel; B, 5% Carbowax 20M on Gaschrom P (80—100), 3.0 m × 3.0 mm stainless steel; C, 5% FFAP on Chromosorb W (80—100) (base washed), 3.0 m × 3.0 mm glass; D, 20% FFAP on Chromosorb W (80—100), 2.6 m × 4.0 mm glass; E, SCOT Carbowax 20M, 58 m × 0.5 mm glass; F, 15% SE30 on

Chromosorb W (60—80), 2.0 m × 6.0 mm glass; and G SCOT Carbowax 20M, 68.6 m × 0.5 mm glass. Products were identified by comparison of their retention times with those of authentic samples and confirmed by peak enhancement. The areas of peaks were determined with either a Perkin-Elmer 194B printing integrator or a disc integrator and were checked by triangulation. Relative response ratios were determined by standard techniques. High performance liquid chromatographic (h.p.l.c.) separations were carried out on a Spectra-Physics 3500B chromatograph equipped with a Spectra-Physics 230 detector and a Pye-Unicam LCM2 detector. Two Lichrosorb S1.60 (10μ, 50 cm × 1 cm) columns were used in series. Silver nitrate impregnated silica was prepared by the procedure of Gream *et al.*[33]

4-*t*-*Butylcyclohexanol*.—A sample of the commercial material after recrystallisation had m.p. 61—65 °C and was shown to be a mixture of the *cis*- and *trans*-isomers (30 : 70) by g.l.c. (column A).

c-4-*t*-*Butyl*-c-2-*methylcyclohexan*-r-1-*ol* (33c) *and* t-4-*t*-*Butyl*-t-2-*methylcyclohexan*-r-1-*ol* (32c).—When 4-t-butyl-2-methylphenol (prepared in 71% yield from 2-methylphenol)[34] was hydrogenated[20] a mixture of the alcohol (33c) (64%) and its isomer (32c) (36%) was obtained in 82% yield. Chromatography of the mixture on alumina afforded *c*-4-t-butyl-*c*-2-methylcyclohexan-*r*-1-ol (33c), homogeneous by g.l.c. (column C; 150 °C; 6.5 min), m.p. 79—81 °C (lit.,[20] 78—79 °C), and *t*-4-t-butyl-*t*-2-methylcyclohexan-*r*-1-ol (32c), homogeneous by g.l.c. (column C; 150 °C; 7.8 min), m.p. 69—70 °C (lit.,[20] 72—73 °C).

c-4-*t*-*Butyl*-t-2-*methylcyclohexan*-r-1-*ol* (35a) *and* t-5-*t*-*Butyl*-t-2-*methylcyclohexan*-r-1-*ol* (35b).—Treatment of a mixture of *cis*-4-t-butylepoxycyclohexane and *trans*-4-t-butylepoxycyclohexane (prepared in 74% yield from 4-t-butylcyclohexene)[35] with dimethylmagnesium[21,22] gave a mixture (57%) of the alcohols (35a and b) [g.l.c. column C; 150 °C; 6.5 min (68%) and 6.9 min (32%)] which were separated by h.p.l.c. [ethyl acetate–light petroleum (1 : 10); 16 ml min^{-1}; 12.5 min (68%) and 13.2 min (32%)]. The first was distilled to give an oil, b.p. 108—109 °C at 15 mmHg, which crystallised from light petroleum in needles (2.3 g, 32%), m.p. 70—72 °C (lit.,[21] 70—71 °C), of *c*-4-t-butyl-*t*-2-methylcyclohexan-*r*-1-ol (35a). The second crystallised from light petroleum in needles (0.9 g, 13%), m.p. 74—76 °C (lit.,[22] 75—76 °C), of *t*-5-t-butyl-*t*-2-methylcyclohexan-*r*-1-ol (35b).

c-4-*t*-*Butyl*-c-2,c-6-*dimethylcyclohexan*-r-1-*ol* (33d).—A solution of 4-t-butyl-2,6-dimethylphenol (10.0 g, prepared in 54% yield from 2,6-dimethylphenol)[36] in 95% aqueous ethanol over 5% rhodium on alumina (1.0 g) was hydrogenated at 2 500 lb in^{-2} and 100 °C for 72 h. The mixture was then filtered through Celite, concentrated, and distilled to give the required *alcohol* as an oil, b.p. 88—90 °C at 4 mmHg, which crystallised from light petroleum as needles (7.5 g, 68%), m.p. 62—63 °C, homogeneous by g.l.c. (column A; 150 °C, 5.45 min) (Found: C, 78.5; H, 12.9. $C_{12}H_{24}O$ requires C, 78.2; H, 13.1%); *m/e* 184 (*M*, 27%), 167 (14), and 109 (100); $\nu_{max.}$ (Nujol) 961, 1 363, and 3 446 cm^{-1}; δ_H 0.86 (9 H, s, Bu^t), 0.92 (6 H, d, *J* 6 Hz, 2 × CH_3), 1.0—2.2 (7 H), 2.35br (1 H, s, OH), and 3.43 (1 H, m, C*H*OH); δ_C 18.8 (2 × CH_3), 27.6 and 32.4 (Bu^t), 28.5 (C-3, C-5; 29.4), 37.4 (C-2, C-6; 38.9), 47.7 (C-4; 48.2), and 74.6 p.p.m. (C-1).

c-4-*t*-*Butyl*-r-2,c-6-*dimethylcyclohexanone*.—Jones' reagent (8N)[37] was added dropwise to a solution of *c*-4-t-butyl-*c*-2,*c*-6-dimethylcyclohexan-*r*-1-ol (5.5 g) in acetone (50 ml) until the colour persisted. The mixture was then poured into water (150 ml) and extracted with ether (3 × 100 ml). The ether extracts were then washed with sodium hydrogencarbonate solution and with water, dried, and distilled to give the required *ketone* as a liquid (5.1 g, 93%), b.p. 95—98 °C at 10 mmHg, homogeneous by g.l.c. (column F; 150 °C; 4.20 min) (Found: C, 78.8; H, 12.1. Calc. for $C_{12}H_{22}O$: C, 79.1; H, 12.1%); *m/e* 182 (*M*, 11%), 126 (56), 57 (100), and 41 (27); $\nu_{max.}$ 1 365 and 1 718 cm^{-1}; δ_H 0.95 (9 H, s, Bu^t), 0.98 (6 H, d, *J* 7.5 Hz, 2 × CH_3), and 1.0—2.6 (7 H); δ_C 14.8 (2 × CH_3; 14.6), 27.7 and 32.4 (Bu^t; 27.6 and 32.4), 38.2 (C-3, C-5; 37.6), 44.3 (C-2, C-6; 44.5), 47.0 (C-4; 47.1), and 215.2 p.p.m. (C-1).

c-4-*t*-*Butyl*-r-2,t-6-*dimethylcyclohexanone*.—A solution of the preceding ketone (4.8 g), semicarbazide hydrochloride (5.6 g), and potassium acetate (5.0 g) in methanol (90 ml) was boiled under reflux for 18 h, then concentrated and diluted with water (100 ml). The resultant precipitate was dried and crystallised twice from methanol to give the semicarbazone as needles (5.2 g, 86%), m.p. 173—174 °C (Found: C, 64.9; H, 10.5. Calc. for $C_{13}H_{25}N_3O$: C, 65.2; H, 10.5%); δ_H 0.90 (9 H, s, Bu^t), 1.10 (6 H, d, *J* 7.5 Hz, 2 × CH_3), 1.4—3.6 (7 H), 6.0br (2 H, s, NH_2), and 8.86br (1 H, s, NH).

A solution of the semicarbazone (5.0 g) in acetic acid (30 ml) was maintained below 5 °C while sodium nitrite (4.2 g) in water (30 ml) was added during 30 min. After extraction of the mixture with ether, the extract was washed with sodium hydrogen carbonate solution and with water, dried, and distilled to afford *c*-4-t-butyl-*r*-2,*t*-6-dimethylcyclohexanone (3.4 g, 89%), b.p. 104—105 °C at 10 mmHg (Found: C, 79.4; H, 12.0. $C_{12}H_{22}O$ requires C, 79.1; H, 12.1%); *m/e* 182 (*M*, 16%), 126 (77), 57 (91), and 41 (100); $\nu_{max.}$ 1 373 and 1 716 cm^{-1}; δ_H 0.86 (9 H, s, Bu^t), 0.95 (3 H, d, *J* 7.5 Hz, equatorial CH_3), 1.12 (3 H, d, *J* 7.5 Hz, axial CH_3), and 1.3—2.8 (7 H); δ_C 15.1 (equatorial CH_3; 14.6), 17.5 (axial CH_3; 17.4), 27.5 and 32.2 (Bu^t; 27.6 and 32.4), 34.1 (C-5; 34.5), 36.3 (C-3; 36.2), 40.6 (C-2; 38.4), 41.3 (C-4; 41.0), 43.4 (C-6; 44.7), and 218.5 p.p.m. (C-1). The ketone was shown by g.l.c. to be contaminated with 1—2% of *c*-4-t-butyl-*r*-2,*c*-6-dimethylcyclohexanone [column F; 150 °C; 4.20 min (*ca.* 2%), 4.55 min (*ca.* 98%)].

t-4-*t*-*Butyl*-c-2,t-6-*dimethylcyclohexan*-r-1-*ol* (32d).—A solution of the preceding ketone (3.1 g) in dry ether (60 ml) was heated with lithium aluminium hydride (1.0 g) under reflux for 3 h. The cooled mixture was then worked-up in the usual way with sodium hydroxide solution, and the crude product was distilled to give the required *alcohol*, b.p. 106—108 °C at 10 mmHg, which crystallised from light petroleum as needles (2.1 g, 69%), m.p. 56—58 °C (Found: C, 78.5; H, 13.1. $C_{12}H_{24}O$ requires C, 78.2; H, 13.1%); *m/e* 184 (*M*, 14%), 167 (8), and 109 (100); $\nu_{max.}$ (Nujol) 1 043, 1 363, and 3 432 cm^{-1}; δ_H 0.86 (9 H, s, Bu^t), 0.92 (6 H, d, *J* 6 Hz, 2 × CH_3), 1.1—2.5 (7 H), 2.2br (1 H, s, OH), and 3.2 (1 H, dd, *J* 5 and 10 Hz, C*H*OH); δ_C 12.2 (equatorial CH_3), 19.1 (axial CH_3), 27.5 and 31.9 (Bu^t; 27.5 and 32.1), 32.1 (C-3; 30.6), 33.1 (C-5; 34.5), 34.6 (C-6; 35.9), 35.3 (C-2; 36.8), 40.1 (C-4; 41.9), and 78.8 p.p.m. (C-1). The alcohol (32d) was shown by g.l.c. to contain *ca.* 1—2% of its isomer (33d) [column A; 150 °C; 5.45 min (*ca.* 2%), 6.50 min (*ca.* 98%)].

cis-1-*Bromo*-4-*t*-*butylcyclohexane*.—A mixture of 4-t-butylcyclohexanol (3.0 g), phosphorus tribromide (5.4 g), pyridine (0.3 ml), and benzene (30 ml) was stirred at 55 °C for 12 h, then cooled, and poured onto ice. The layers were separated, the aqueous solution was extracted with benzene, and the combined organic extracts were washed with sodium carbonate solution and with water, dried, and distilled to give the required

bromide (3.5 g, 84%), b.p. 112—114 °C at 19 mmHg (lit.,[16] 104—110 °C at 14 mmHg).

trans-4-*t*-*Butylcyclohexanecarboxylic Acid*.—The Grignard reagent prepared from the preceding bromide (2.2 g), magnesium (0.48 g), and ether (50 ml) was poured onto solid carbon dioxide (12 g). After acidification of the mixture the organic phase was separated and the aqueous solution was extracted twice with ether. After being washed with water the combined ether solutions were extracted thrice with saturated sodium hydrogencarbonate solution. Acidification of the aqueous extracts gave a precipitate of the required carboxylic acid which crystallised from ethanol in plates (0.95 g, 52%), m.p. 176—178 °C (lit.,[15] 174—176 °C).

t-4-*t*-*Butyl*-t-2-*methylcyclohexane*-r-1-*carboxylic Acid* (32a), c-4-*t*-*Butyl*-c-2-*methylcyclohexane*-r-1-*carboxylic Acid* (33a), *and* t-4-*t*-*Butyl*-c-2-*methylcyclohexane*-r-1-*carboxylic Acid* (34).—4-t-Butyl-2-methylcyclohexanone [17] was converted as previously described [18] into a mixture of the three acids (32a), (33a), and (34), which was converted into a mixture of the appropriate methyl esters, and separated by h.p.l.c. Hydrolysis of the fractions [18] afforded pure samples of the acids (32a), (33a), and (34) having physical and spectral properties identical with those previously reported.[18]

c-5-*t*-*Butyl*-1,r-3-*dimethylcyclohexene* (27).—(a) A solution of the alcohol (33d) (1.0 g) in pyridine (20 ml) was stirred at < -5 °C while thionyl chloride (4 ml) was added dropwise. After being kept at -5 °C for 4 h the mixture was poured onto ice, extracted with ether, and worked up in the usual way to give an oil which was chromatographed on alumina. The fraction eluted with light petroleum was distilled to afford the *olefin* (27) (0.54 g, 60%), b.p. 45—47 °C (block) at 15 mmHg, homogeneous by g.l.c. (column E; 100 °C; 31.3 min) (Found: C, 86.5; H, 13.4. $C_{12}H_{22}$ requires C, 86.7; H, 13.3%); *m/e* 165 ($M - 1$, 100%) and 57 (42); δ_H 0.90 (9 H, s, Bu^t), 0.94 (3 H, d, *J* 8.5 Hz, CH_3), 1.70 (3 H, m, allylic CH_3), 1.2—2.6 (6 H), and 5.20 (1 H, m, vinylic CH); δ_C 22.2 (CH_3; 22.4), 23.7 (allylic CH_3; 23.8), 27.3 and 32.4 (Bu^t; 27.7 and 32.7), 31.8 (C-6; 31.6), 32.4 (C-3; 32.3), 33.6 (C-4; 33.7), 44.8 (C-5; 45.5), 127.9 (C-2), and 133.7 p.p.m. (C-1).

(b) Treatment of the alcohol (33d) (3.9 g) with toluene-*p*-sulphonyl chloride (7.2 g) in pyridine (50 ml) at 0—3 °C for 30 h in the usual way afforded *c*-4-t-butyl-*c*-2,*c*-6-dimethylcyclohexyl *r*-toluene-*p*-sulphonate (33h) which crystallised from light petroleum at -78 °C in needles (1.7 g, 63%), m.p. 117—118 °C; δ_H 0.87 (9 H, s, Bu^t), 0.98 (6 H, d, *J* 7 Hz, 2 × CH_3), 1.1—2.3 (7 H), 2.50 (3 H, s, $ArCH_3$), 4.9 (1 H, m, CHOTos), and 7.3—8.1 (4 H, m, ArH). A solution of this tosylate (0.65 g) in dimethyl sulphoxide (2 ml) and benzene (10 ml) was added dropwise to a stirred suspension of potassium t-butoxide (0.5 g) in dimethyl sulphoxide (8 ml), and the mixture was stirred for 16 h at ambient temperature, and then poured into ice–water. Extraction with pentane and distillation of the extract afforded the olefin (27) (0.13 g, 41%).

(c) The alcohol (33d) (6.2 g) was heated with acetic anhydride (15 ml) and pyridine (15 ml) at 50 °C for 6 h, and the mixture was worked up in the usual way to give *c*-4-t-butyl-*c*-2,*c*-6-dimethylcyclohexyl *r*-acetate (33g) (4.7 g, 61%), b.p. 141—144 °C at 18 mmHg, homogeneous by g.l.c. (column D; 100 °C; 3.30 min); δ_H 0.87 (9 H, s, Bu^t), 0.93 (6 H, d, *J* 6.5 Hz, 2 × CH_3), 1.1—2.6 (7 H), 2.10 (3 H, s, $OCOCH_3$), and 4.90 (1 H, m, CHOAc). This acetate (2.0 g) was slowly distilled at 15 mmHg through a Vycor tube (50 cm × 2.5 cm) packed with silica beads and maintained at 475 °C. The pyrolysate, which was collected in a trap at -78 °C, was taken up in light petroleum, washed with sodium carbonate solution and with water, dried, and distilled to afford the olefin (27) (0.68 g, 47%).

t-5-*t*-*Butyl*-1,r-3-*dimethylcyclohexene* (29).—The alcohol (32d) was converted as described above into its acetate (32g) (68%), b.p. 130—135 °C at 15 mmHg; δ_H 0.88 (9 H, s, Bu^t), 0.90 (3 H, d, *J* 8 Hz, equatorial CH_3), 0.93 (3 H, d, *J* 8 Hz, axial CH_3), 1.0—2.5 (7 H), 2.00 (3 H, s, $OCOCH_3$), and 4.42 (1 H, dd, *J* 4.5 and 11 Hz, CHOAc). The acetate (32g) was shown by g.l.c. to be contaminated with 1—2% of the acetate of the alcohol (33d) [column D; 100 °C; 3.30 min (*ca.* 2%) and 3.75 (*ca.* 98%)]. Pyrolysis of this acetate (see preceding experiment) gave the *olefin* (29) (51%), b.p. 47—48 °C (block) at 20 mmHg (Found: C, 86.3; H, 13.2. $C_{12}H_{22}$ requires C, 86.7; H, 13.3%); *m/e* 165 ($M - 1$, 52%) and 57 (100); δ_H 0.89 (9 H, s, Bu^t), 0.95 (3 H, d, *J* 9 Hz, CH_3), 1.1—2.6 (6 H), 1.68 (3 H, m, allylic CH_3), and 5.35 (1 H, m, vinylic H); δ_C 21.0 (CH_3), 24.0 (allylic CH_3; 23.8), 27.4, and 32.2 (Bu^t; 27.7 and 32.7), 30.0 (C-4; 30.0), 30.4 (C-3; 27.8), 32.2 (C-6; 31.8), 39.1 (C-5; 40.1), 126.9 (C-2), and 133.5 p.p.m. (C-1). The sample was shown by g.l.c. to contain 7% of the isomer (27) [column E; 100 °C; 31.3 min (7%) and 32.2 min (93%)].

(b) Treatment of the alcohol (32d) with thionyl chloride in pyridine as described above gave a mixture (0.24 g, 47%), b.p. 109—110 °C (block) at 13 mmHg, of the olefins (27) and (29) [column E; 100 °C; 31.3 min (93%) and 32.2 min (7%)].

(c) The toluene-*p*-sulphonate (32h), prepared in the usual way from the alcohol (32d), was obtained as a crystalline solid (1.65 g, 24%), m.p. 103—104 °C (decomp.); δ_H ($CDCl_3$) 0.90 (9 H, s, Bu^t), 1.04 (6 H, d, *J* 7.5 Hz, 2 × CH_3), 1.1—2.3 (7 H), 2.54 (3 H, s, $ArCH_3$), 4.35 (1 H, dd, *J* 5.5 and 11 Hz, CHOTos), and 7.3—8.1 (4 H, m, ArH). On treatment with potassium t-butoxide as described above it afforded a mixture (0.17 g, 34%), b.p. 50—55 °C (block) at 18 mmHg, of the olefins (27) and (29) [column E; 100 °C; 31.3 min (91%) and 32.2 min (9%)].

c-5-*t*-*Butyl*-r-3-*methylcyclohexene* (28) *and* 5-*t*-*Butyl*-1-*methylcyclohexene* (25).—(a) Treatment of a mixture of *c*-4-t-butyl-*c*-2-methylcyclohexan-*r*-1-ol (33c) (64%) and *t*-4-t-butyl-*t*-2-methylcyclohexan-*r*-1-ol (32c) (36%) with thionyl chloride and pyridine as described above afforded a mixture of two components [column G; 100 °C; 28.0 min (8%) and 32.4 min (92%)] which was chromatographed on silver nitrate impregnated silica. Elution with light petroleum gave 5-t-butyl-1-methylcyclohexene (25) (1.7 g, 54%), b.p. 59—63 °C at 20 mmHg (lit.,[38] 82.0—82.5 °C at 18 mmHg), homogeneous by g.l.c. (column G; 100 °C; 32.4 min). Continued elution with light petroleum afforded *c*-5-t-butyl-*r*-3-methylcyclohexene (28) (0.13 g, 4%), b.p. 60—62 °C (block) at 20 mmHg (lit.,[31] 85—87 °C at 35 mmHg), also homogeneous by g.l.c. (column G; 100 °C; 28.0 min).

(b) Treatment of a mixture of the alcohols (33c) (64%) and (32c) (36%) with toluene-*p*-sulphonyl chloride as described above gave a mixture of the toluene-*p*-sulphonates (33f) (64%) and (32f) (36%) as a crystalline solid (1.46 g, 35%), m.p. 52—59 °C (decomp.); δ_H ($CDCl_3$) 0.88 (9 H, s, Bu^t), 1.02 (3 H, d, *J* 7 Hz, CH_3), 1.0—2.1 (8 H), 2.53 (3 H, s, $ArCH_3$),4. 40 (0.36 H, m, $CH_{axial}OH$), 4.85 (0.64 H, m, $CH_{equatorial}OH$), and 7.3—8.1 (4 H, m, ArH). Treatment of this mixture with potassium t-butoxide afforded a mixture of the cyclohexenes (25) and (28) [column G; 100 °C; 28.0 min (12%) and 32.4 min (88%)] as an oil (0.24 g, 52%), b.p. 43—49 °C (block) at 12 mmHg, which were separated by chromatography on silver nitrate-impregnated silica.

(c) Acetylation of a mixture of the alcohols (33c) (64%) and (32c) (36%) in the usual way gave a mixture of the acetates (33e) and (32e) as an oil (3.7 g, 73%), b.p. 126—129 °C at 19

mmHg [column D; 100 °C; 3.1 min (64%) and 3.6 min (36%)], pyrolysis of which afforded a mixture of the olefins (28) (32%) and (25) (88%) as an oil (1.3 g, 72%), b.p. 51—52 °C at 16 mmHg. Chromatography of the mixture on silver nitrate-impregnated silica afforded the separate components.

t-5-*t-Butyl*-r-3-*methylcyclohexene* (30).—Treatment of the alcohol (35a) with toluene-*p*-sulphonyl chloride in the usual way gave the toluene-*p*-sulphonate (35c) which was stirred with potassium t-butoxide as described above to give a mixture of two components [column G; 100 °C; 28.8 min (33%) and 32.4 min (67%)] which was chromatographed on silver nitrate impregnated silica. Elution with light petroleum gave the major fraction, 5-t-butyl-1-methylcyclohexene (25) as an oil (17%), b.p. 63—67 °C (block) at 18 mmHg. Further elution gave the minor fraction, *t*-5-t-butyl-*r*-3-methylcyclohexene (30) as an oil (6%), b.p. 51—57 °C (block) at 16 mmHg (lit.,[31] 63 °C at 10 mmHg).

r-3-*t-Butyl*-c-6-*methylcyclohexene* (31) *and* 4-*t-Butyl*-1-*methylcyclohexene* (26).—Acetylation of the alcohol (35b) in the usual way afforded the corresponding acetate which was subjected to flash pyrolysis as described above to afford a mixture of two components [column G; 100 °C; 29.7 min (42%) and 33.5 min (58%)]. The major component (24%) separated by chromatography on silver nitrate-impregnated silica was 4-t-butyl-1-methylcyclohexene (26), b.p. 50—57 °C (block) at 17 mmHg (lit.,[39] 180—182 °C at 752 mmHg). The minor component (19%), similarly isolated, was the olefin (31), b.p. 62—64 °C (block) at 25 mmHg, which had spectral properties identical with those previously reported.[40,41]

t-Butylcyclohexane.—4-t-Butylcyclohexene[42] (1.0 g) in acetic acid (15 ml) was shaken with platinum oxide (0.3 g) under hydrogen at 50 lb in^{-2} for 12 h. The mixture was then filtered through Celite, and the filtrate was diluted with water (40 ml) and extracted thrice with light petroleum. The combined extracts were washed with sodium hydrogencarbonate solution and with water, dried, and distilled to afford t-butylcyclohexane (0.68 g, 67%), b.p. 69—72 °C at 15 mmHg (lit.,[43] 172 °C at 760 mmHg), homogeneous by g.l.c. (column E; 100 °C; 18.6 min).

r-1-*t-Butyl*-c-4-*methylcyclohexane* (19).—Hydrogenation of *r*-3-t-butyl-*c*-6-methylcyclohexene (31) as described above gave the cycloalkane (19), b.p. 76—82 °C (block) at 14 mmHg (lit.,[44] 189 °C at 760 mmHg), homogeneous by g.l.c. (column G; 100 °C; 26.0 min).

r-1-*t-Butyl*-c-3-*methylcyclohexane* (21).—Hydrogenation of the cycloalkene (28) as described above gave the cycloalkane (21), b.p. 77—80 °C (block) at 17 mmHg (lit.,[38] 75 °C at 20 mmHg), homogeneous by g.l.c. (column G; 100 °C; 23.0 min).

r-1-*t-Butyl*-t-3-*methylcyclohexane* (23).—Similar treatment of *t*-5-t-butyl-*r*-3-methylcyclohexene (30) gave the cycloalkane (23), b.p. 70—75 °C (block) at 15 mmHg (lit.,[26] 163—175 °C at 760 mmHg), homogeneous by g.l.c. (column G; 100 °C; 25.3 min).

r-1-*t-Butyl*-c-3,*c*-5-*dimethylcyclohexane* (20) *and* r-1-*t-Butyl*-c-3,t-5-*dimethylcyclohexane* (22).—(a) Hydrogenation of *c*-5-t-butyl-1,*r*-3-dimethylcyclohexene (27) as described above gave a mixture (76%) of the cycloalkanes (20) (89%) and (22) (11%) as an oil, b.p. 78—80 °C (block) at 20 mmHg (Found: C, 85.7; H, 14.5. $C_{12}H_{24}$ requires C, 85.6; H, 14.4%); δ_H 0.87 (9 H, s, Bu^t), 0.90 (6 H, d, *J* 9 Hz, 2 × CH_3), and 0.95—2.4 (9 H).

(b) Similar treatment of *t*-5-t-butyl-1,*r*-3-dimethylcyclohexene (30) gave a mixture (79%) (Found: C, 85.3; H, 14.5%) containing the olefins (20) (12%) and (22) (88%).

General Procedure[11] *for the Preparation and Thermolysis of Alkyl t-Butylperoxyoxalates*.—The appropriate cyclohexanol (1 mmol) was added in small portions over *ca.* 10 min to oxalyl chloride (2 mmol) under nitrogen at 0 °C. When the addition was complete the reaction mixture was allowed to warm to room temperature, excess oxalyl chloride was removed under reduced pressure, and the residue was distilled to give the chloroglyoxalate as an oil which was stored in the dark.

A solution of t-butyl hydroperoxide (0.5 mmol) and pyridine (0.5 mmol) in cyclohexane (1 ml) was kept below 0 °C during the dropwise addition of a solution of the chloroglyoxalate (0.5 mmol) in cyclohexane (1 ml). Pyridine hydrochloride began to precipitate immediately. When the addition was complete the solution was allowed to warm to room temperature and was then filtered. The residue was washed with cyclohexane (1 ml) and the combined cyclohexane solutions were placed in an ampoule, flushed with nitrogen, then sealed under nitrogen and heated at 100 °C for 2 h. The ampoule was then cooled in ice, opened, and an accurately weighed sample of an internal standard [one of the cyclohexanes (18)—(23)] was added. Each experiment was performed at least in duplicate.

Products were identified by comparison of their g.l.c. retention times with those of authentic samples on columns B, E, and G. For accurate calculation of yields molar response ratios were determined. Each analysis was performed at least in triplicate. Yields calculated by repeated analyses varied by $<2\%$.

Mixtures were also analysed by comparison of physical and spectral properties of components separated by chromatography on silver nitrate-impregnated silica with those of authentic samples. Elution with light petroleum gave the appropriate cyclohexane. Continued elution with light petroleum gave the cyclohexene(s). When more than one cyclohexene was produced the one with the most substituted double bond eluted first. The cyclohexenes (27) and (29) formed in the reaction of the peroxide (4) could not be separated.

General Procedure[14] *for the Preparation and Thermolysis of Diacyl Peroxides*.—The appropriate carboxylic acid (5 mmol) and thionyl chloride (15 mmol) were heated under reflux for 0.5 h. Excess thionyl chloride was removed under reduced pressure and the residue was distilled to give the acid chloride as an oil.

To a suspension of sodium peroxide (1.3 mmol) in anhydrous ether (3 ml) a solution of the acid chloride (2 mmol) in ether (1 ml) was added. Reaction was initiated by adding a drop of water and was assumed to be complete when the yellow colour of the peroxide had disappeared and the addition of water no longer caused the temperature to rise. Cold water (5 ml) was then added, the ether layer was separated and washed with 10% aqueous sodium carbonate, dried ($MgSO_4$) and concentrated under reduced pressure at 0 °C. Cyclohexane (2 ml) was added to the residue and the resultant solution was placed in an ampoule, flushed with nitrogen, sealed under nitrogen, and heated at 100 °C for 2 h. The mixture was then cooled and analysed as described above.

Solvolysis of t-4-*t-Butyl*-c-2,t-6-*dimethylcyclohexyl* r-*Toluene*-p-*sulphonate* (32h).—A solution of the toluene-*p*-sulphonate (0.5 g) and anhydrous sodium acetate (0.25 g) in anhydrous acetic acid (15 ml) was heated in a sealed ampoule under nitrogen at 75 °C for 8 h, then cooled, diluted with

water (40 ml), and extracted thrice with light petroleum. The combined extracts were washed with sodium hydrogencarbonate solution and with water, dried, and concentrated. Analysis of the residue by g.l.c. (column E; 100 °C) showed it to contain *c*-5-t-butyl-1,*r*-3-dimethylcyclohexene (27) (47%) and two unidentified components [27.7 (36%) and 29.6 min (17%)].

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