Studies in Carbonium Ion Chemistry

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by

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The meso-hydrobenzoin sulphites (94-96) have been prepared and in each case the stereo-isomers separated. Pyrolysis of these cyclic sulphites gave mixtures of aldehyde and ketone. For any pair of sulphites the product ratio has been shown to be dependent on the stereochemistry of the S-0 bond, a greater yield of ketone being produced when the S-0 is syn to a hydrogen on the heterocyclic ring. This is thought to be due to abstraction of the hydrogen by the syn S-0 to form the enol of a ketone. The differences between the aldehyde to ketone ratios for a series of S-0 isomers, where the aryl substituent changes, has been rationalized in terms of the migratory aptitude of the aryl group.

The product ratios obtained when the unsubstituted (31), 1-methyl (33), 2-methyl (42) and 1,2-dimethyl (45) alkenes are oxidized by KMnO₄, performic acid and iodine-silver acetate-water are discussed. The products from these oxidations are the substituted cyclohexane-1,2-diols (46-57; 60-63). The cyclic sulphites of these diols have been prepared and the isomers separated. Pyrolysis of the cyclic sulphites produced aldehyde and(or) ketones. The products result from a 1,2-hydride, methyl or methylene shift.
In only one case was a cis-1,2-hydride shift observed, implying a considerable degree of charge separation in the transition state. The major product arises from a 1,2-hydride shift where a favourable conformation is available.
INTRODUCTION

Carbonium ion rearrangements involving 1,2-alkyl migrations are a specific example of anionotropic rearrangements\(^1\) where the migrating group carries its electron pair with it. In its simplest terms the overall reaction may be represented as in Fig.1.

There are three distinct processes: (i) ionization of the C-X bond, (ii) migration of the group R and (iii) collapse of the rearranged ion to the reaction products. The relative timing of the processes allows the possibility of three mechanistic schemes\(^2\) as illustrated by the energy diagrams (Fig. 2a-2c).

(a) Migration occurs before the ionization is complete implying migration to be synchronous with rupture of the C-X bond. The electron deficient centre is stabilized by the electrons of the migrating group and the reaction is similar to an SN2 reaction where the migrating group R is the attacking nucleophile. The participation of the migrating group lowers the energy of the transition state.

(b) Migration occurs sequential to ionization of the C-X bond but before complete separation of the anion from the carbonium ion. The migrating group must be in the plane of the vacant lobe of the carbonium ion and trans to
the departing X group.

(c) Migration of R occurs to a stable carbonium ion completely separated from its anion. The stereoelectronic requirement of a trans migrating group need not operate and cis-migration will occur as readily as trans.

The normally accepted$^2$ stereoelectronic requirement of the carbonium ion rearrangement necessitates the migrating group to be trans and coplanar to the leaving group. The exception is when the carbonium ion is sufficiently stable to survive without its anion (reaction type C).

For six membered rings this leads to the anti-coplanar or trans-coplanar arrangement of the four atoms involved in the reaction. The possible reaction paths$^2$ complying with requirement are shown in Fig. 3.

The generality of this principle has been well illustrated in steroid systems$^2$ having a rigid ring structure. Deamination$^3$ of the four isomeric 4-tert-butyl-2-aminocyclohexanols similarly serves to illustrate these principles, resulting in a high yield (>95%) of the predicted product. (Fig. 4).

When the molecule has two potential migrating groups the choice as to which one migrates is often dependent on fine structural details and(or) the conditions under which the reaction is carried out. However most frequently the migrating order is hydrogen>aryl>alkyl but mixtures are found.
The relative migratory aptitudes of alkyl groups, in the pinacol rearrangement, have been established\(^a\) to be: tert-butyl, 4000; ethyl, 17; methyl, 1.

For aryl groups electron donating substituents increase the migratory aptitude while electron withdrawing substituents decrease the migratory aptitude. Groups in the ortho position often decrease the tendency to migrate, but this is considered to be due to steric effects.

The following relative migratory aptitudes were determined by examining the pinacol rearrangement of appropriately substituted symmetrical glycols\(^1\): p-anisyl; 500; p-tolyl; 15.7; m-tolyl; 1.95; phenyl; 1.0; p-chlorophenyl; 0.7; o-anisyl; 0.3. There is, as might be expected, some correlation between the migratory aptitude and the reactivity toward electrophilic substitution.

Free radical rearrangements are much less common than carbonium ion rearrangements.\(^1,5\) When they do occur a mechanistic scheme applies similar to that for carbonium ion rearrangements (fig. 5).

In general 1,2-alkyl shifts and 1,2-hydrogen migrations are not observed in free radical reactions.\(^1,5\) 1,3-Hydrogen and longer migrations do occur (1,5 being favoured) but these are considered to be internal hydrogen abstractions.\(^1\) Aryl migrations do occur and the migration can be regarded as an internal aromatic substitution reaction.\(^6\) These groups most susceptible to radical substitution are the
most likely to migrate. The selectivity of migrating group is much smaller than that found in carbonium ion aryl migrations, with a p-methyl substituent having little effect on the aryl migratory aptitude. A more marked increase in migrating tendency is noted for p-nitrophenyl, napthyl and biphenyl groups which stabilize the radical by delocalization.

This thesis is largely concerned with 1,3-dioxa-2-thiolane 2-oxides (3) and the rearrangement reactions resulting from the pyrolysis of these compounds.

Organic sulphites are formally the diesters of sulphurous acid, \((\text{HO})_2\text{SO}_3\). The esters are characterized by a sulphite group \((\text{SO}_3^\text{-})\) linked to an organic skeleton by two C-O bonds (1).

The sulphites can be divided into three classes: (i) symmetrical sulphites where the organic radicals (\(R\) and \(R^1\) in 1.) are the same, (ii) asymmetrical sulphites where the organic radicals are different and (iii) cyclic sulphites where the sulphite group forms a heterocyclic ring. Most common of the cyclic sulphites are the 6-membered rings (2) and the 5-membered rings (3) having the names 1,3-dioxa-2-thiane 2-oxides (2) and 1,3-dioxa-2-thiolane 2-oxides (3). Systematic nomenclature will not be used, but rather the compounds will be named as the cyclic sulphite of the diol concerned e.g. 4,5-diphenyl 1,3-dioxa-2-thiane 2-oxide becomes hydrobenzoin cyclic sulphite.
Organic sulphites are prepared by the action of thionyl chloride on the alcohol (or diol), the reaction proceeding via the chlorosulfinate ester of the alcohol (Fig.6.).

The conditions used in the formation of cyclic sulphites depend on the sensitivity of the diol to acid. Pyridine is often used as a means of removing the hydrogen chloride liberated in the reaction. However, the effect of pyridine on the reaction is in doubt, particularly in the preparation of 1,3-glycol sulphites where conflicting results on the use of pyridine have been reported. An alternative is to use a solvent in which hydrogen chloride is only slightly soluble, or to reflux the solution to drive out the hydrogen chloride liberated.

The SO₃ group in cyclic sulphites is non-planar, making unsymmetrical cyclic sulfites isomeric at sulfur. In 1,3-dioxo-2-thiane 2-oxides (2) the S=O can occupy an axial (4) or equatorial position (5). All the evidence from equilibration, dipole moment, and x-ray crystallographic studies indicates that the S=O prefers to occupy the axial position (4). The reason for this is not known.

1,3-Dioxo-2-thioline 2-oxides (3) exist in a slightly puckered 5-membered ring. The puckering had been postulated on the basis of NMR and dipole moment measurements and calculations, and has been confirmed by an x-ray crystal structure of a cyclic sulphite isomer (7a) of
10β-pinane-2, 3α-diol(6).

Cyclic sulphites of the general structure (8) can exhibit isomerism (8a-8d) and several examples have been cited in the literature.

The assignment of the S=O as syn or anti to R can often be made on the basis of the NMR spectra. The proximity of the S=O has a considerable deshielding effect on the position of adjacent protons and methyl groups. There has been some debate as to whether the S=O has an anisotropy effect similar to a carbonyl\(^20\) or to an acetylenic linkage\(^{24,25,26}\). The confusion has been caused in part by failure to distinguish between the anisotropy effect and the proximity effect of the S=O dipole\(^{26,27}\). It would seem that protons (or methyl groups) syn to the S=O resonate at lower field than protons anti to the S=O bond\(^{22,27}\). The evidence suggests that a S=O double bond has a shielding effect similar to an acetylenic linkage\(^{27}\).

The deshielding effect of a syn S-O is illustrated below by the NMR spectra of the sulphite isomers (7a) and (7b)\(^{22}\) and the isomeric sulfoxides\(^{26}\) (9a) and (9b).

<table>
<thead>
<tr>
<th>Compound</th>
<th>10Me (ppm)</th>
<th>3H (ppm)</th>
<th>6H (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a (S=O and R syn)</td>
<td>1.82 ppm</td>
<td>4.94 ppm</td>
<td></td>
</tr>
<tr>
<td>7b (S=O and R anti)</td>
<td>1.46 ppm</td>
<td>4.72 ppm</td>
<td></td>
</tr>
<tr>
<td>9a (S=O and H6 syn-axial)</td>
<td>6.10 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9b</td>
<td></td>
<td>5.29 ppm</td>
<td></td>
</tr>
</tbody>
</table>
The structure of (7a)$_{22}$ and (9b)$_{28}$ was established by x-ray crystallography. This marked effect of the S=O has been used to assign the isomers in various types of S=O containing compounds.$^{27,29}$

Denivelle$^{30}$ reported the thermal rearrangement of butane-1,2-diol cyclic sulphite(10) to give the 2,3-epoxide and butan-2-one. Lewis$^{31,23}$ examined the pyrolysis of the dl- and meso-butane-2,3-diol cyclic sulphites (10a) and (10b).

The cis-sulphite (10b) (from the meso-diol) gave an essentially quantitative yield of butanone containing only a trace (1%) of isobutyraldehyde. The trans-sulphite (10a) (from the dl-diol) gave a mixture (9:1) of butanone and isobutyraldehyde. The products arise from a 1,2-hydride or a 1,2-methyl migration.

The pyrolysis of 10β-pinane-2, 3-diol cyclic sulphite(7) (a 1:1 mixture of 7a and 7b) has been reported$^{32}$ to give a mixture (98:2) of pinocamphone (11) and 2,2,3-trimethylcyclopent-3-en-1-acetaldehyde (12).

Lewis acid (anhydrous HgBr$_2$) catalysed rearrangement$^{32}$ of α-pinene oxide (13) gives essentially pure aldehyde (12). This marked difference for these two reactions, both of which involve cleavage of the C2=S=O bond to give a carbonium ion, has been regarded as a consequence of the different geometry of the epoxide and cyclic sulphite system. During the ionisation of the C2=S=O bond in the sulphite pyrolysis,
the molecule can adopt a conformation(14) in which the \( \beta \)-H is in a favourable position for migration. This flexibility is not available to the reacting molecule in the expoxide intermediate(15), due to the requirement of maximum overlap between the departing oxygen and the developing carbonium ion. Consequently the carbonium ion collapses to the aldehyde(12).

The pyrolysis of 10\( \beta \)-pinane-2, 10-diol cyclic sulphite(16)\(^3\) gave only low yield of a mixture (2:1) of \( p \)-cymene(17) and \( \alpha,\alpha \)-dimethylstyrene(18).

Price and Berti\(^7\) studied the thermal rearrangement of the cyclic sulphites from meso- and dl-hydrobenzoins. The cis-sulphite(19) (from the meso-diol) gave deoxybenzoin(21), whereas the trans-sulphite(22) (from the dl-diol) gave diphenylacetalddehyde(24).

These results were rationalized in terms of bridged ion intermediates(20) and (23) with the subsequent abstraction of a proton by the sulphinate group leading to products. It is assumed the abstraction of a \( \beta \)-proton in(23), is favoured over abstraction of an \( \alpha \)-proton, since the intermediate in the former involves a six-membered ring whereas the latter (\( \alpha \)-proton abstraction) involves a five-membered ring.

Pritchard and Funke\(^3\) pyrolysed meso- and dl-hydrobenzoin cyclic sulphites in the inlet of a mass spectrograph, and analysed the products by examination of the mass spectrum.
of the mixture. The cis-cyclic sulphite(19) gave desoxybenzoin(21) (57%) and diphenylacetaldehyde(24) (41%) whereas the trans-cyclic sulphite(22) gave desoxybenzoin(15%) and diphenylacetaldehyde(66%). Both cyclic sulphite isomers gave small amounts of stilbene (2% and 10% respectively).

Pyrolysis of cis- and trans-cyclohexane diol cyclic sulphites(25) and (26) gave cyclohexanone and cyclopentanone respectively. These results were explained in terms of ring opening and alkyl or hydride shift. In the cis-isomer(25) the hydride shift is favoured since the hydrogen atom is trans and coplanar to the axial C-O bond (assuming cleavage of the axial bond). In the case of the trans-isomer(26) cleavage of either bond will result in alkyl migration.
DISCUSSION.

Preparation and rearrangement of the cis-hydrobenzoin cyclic sulphonites (94-97).

Benzoin(83), 4, 4'-dimethyl-(84) and 4, 4'-dimethoxy-benzoin (85) were prepared by the addition of freshly distilled aldehyde (benzaldehyde, tolylaldehyde and p-methoxy benzaldehyde) to a solution of KCH in EtOH - water and heating under reflux for 5 hours. If the product failed to crystallise from the reaction mixture on cooling, a small portion was extracted with Et₂O and the crude solid obtained used to seed the remainder of the reaction mixture. 3, 3'-Dichlorobenzoin(86) was prepared by adding a saturated aqueous solution of KCH to a solution of freshly distilled m-chlorobenzaldehyde in MeOH and heating under reflux for 30 minutes. The benzoin(86) was isolated by means of Et₂O.

The crystalline benzoins(83-86) were reduced to the meso-hydro-benzoins(89-92) by reduction with NaBH₄ in MeOH. Examination of molecular models of the benzoins indicates that attack from the least hindered side of the more favourable rotomers leads to products with the meso-configuration.

The dinitro-hydrobenzoin(93) may not be prepared by reduction of the benzoin, since p-nitrobenzaldehyde does not undergo a Benzoin Condensation. This compound was prepared by nitration of the diacetate of hydrobenzoin(87) followed by hydrolysis.
Reaction of the hydrobenzoins(89-93) with SOCl₂ led usually to the cyclic sulphite. However the dimethoxyhydrobenzoin(91) gave meso- 4',4' -dimethoxy stilbene dichloride(98). The dimethylhydrobenzoin(90) gave a similar product but by careful choice of conditions the cyclic sulphite could be obtained in moderate yield.

The crude sulphites consisted of a mixture (ca:20:1) of two cyclic sulphite isomers. Crystallization from Et₂O-pentane or EtOH gave the major product assigned in each case the syn-configuration (Fig. 7) on the basis of the known deshielding effect (NMR) of the S-O bond (Table 1.). The anti-isomer (Fig. 7) was isolated by chromatography (silica) of the crystallization residues. The anti-isomer of the dinitro-sulphite(97) was not isolated.

Table 1. The proton chemical shifts for the syn- and anti-isomers of the hydrobenzoin sulphites(94-97).

<table>
<thead>
<tr>
<th></th>
<th>syn-isomer ppm</th>
<th>anti-isomer ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(96) X, 3-chloro</td>
<td>6.13</td>
<td>5.83</td>
</tr>
<tr>
<td>(94) X, H</td>
<td>6.12</td>
<td>5.79</td>
</tr>
<tr>
<td>(95) X, 4-methyl</td>
<td>6.10</td>
<td>5.77</td>
</tr>
<tr>
<td>(97) X, 4-nitro</td>
<td>6.38</td>
<td>6.05</td>
</tr>
</tbody>
</table>
Pyrolysis of the syn- and anti-sulphites (94–96) by heating for 20 minutes under nitrogen gave mixtures of the corresponding aldehyde and ketone (>80%) together with traces of several minor products. The pyrolysis of the dinitro-sulphite (97) gave a dark viscous oil in which no products could be identified. The pyrolysis products were identified (IR, NMR) after being isolated from the product mixture by preparative GLC. The only product which could not be isolated was di-m-chlorophenyl acetaldehyde.

The effect of the phenyl substituent on the reaction course (Table 2) follows the trend expected for a heterolytic process, there being greater extent of aryl migration in the presence of electron donating substituents. Homolytic migration preferences are only observed for those groups capable of stabilizing the free radical by delocalization\textsuperscript{5,6} i.e. p-nitrophenyl, naphthyl and biphenyl. Furthermore p-methyl has little or no effect on migration tendency in homolytic processes\textsuperscript{5,6}.

The formation of aldehyde from these meso-sulphites cannot be rationalized in terms of a bridged ion intermediate (20) with subsequent proton abstraction as postulated by Price and Berti\textsuperscript{7}. An α-hydrogen abstraction leads to ketone products, while aldehyde formation requires the abstraction of a trans-β-hydrogen. If the product ratios were dependent on the
relative accessibility of the $\alpha$- and $\beta$-protons in 20, then the aryl substituent should have little effect on the product distribution.

Table 2. Product ratios from the pyrolysis of the syn- and anti-hydrobenzoin cyclic sulphites.

<table>
<thead>
<tr>
<th>Sulphite</th>
<th>Ketone (XG_6H_4CH_2COG_6H_4X(99-101))</th>
<th>Aldehyde (XG_4H_2^-CHCHO(102-104))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,3-Dichloro(96)</td>
<td>syn - 82</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>anti - 64</td>
<td>36</td>
</tr>
<tr>
<td>H(94)</td>
<td>syn - 64</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>anti - 33</td>
<td>67</td>
</tr>
<tr>
<td>4,4-Dimethyl(95)</td>
<td>syn - 36</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>anti - 15</td>
<td>85</td>
</tr>
</tbody>
</table>

The mechanistic rationale proposed is cleavage of the Cl-O bond and rotation of C2 to align the aryl or hydrogen favourably for migration (Fig. 8). For the series of cis-sulphites examined (94–97) the steric factors are approximately constant and the observed product ratios are thus dependent on the electronic nature of the aryl group. The proportion of aldehyde product increases with increasing migration tendency of the aryl group.
The marked effect of the stereochemistry about the sulphur atom (Table 2) is due to an alternative reaction pathway available when the S-0 and hydrogen occupy a syn-relationship. This mechanism involves abstraction of the hydrogen by the syn S-0 to produce an enol intermediate (116) which then collapses to the ketone (Fig. 9).

This enol-mechanism is an alternative reaction pathway available only to the syn-sulphite isomers. Cyclic sulphites and sulphoxides can be equilibrated thermally and with mineral acid. However thermal equilibration of the sulphoxide isomers (117 and 118) was found to be slow and accompanied by decomposition. The effect of the S-0 stereochemistry on the product ratios indicates that little equilibration is occurring before pyrolysis.

A further example of the effect of the S-0 orientation on the course of pyrolysis was observed by Lewis (23) in the pyrolysis of the 2-phenylbornane-2,3-exo-diol cyclic sulphites (119 and 120). The sulphite isomer (119) with the 3-endo-hydrogen and S-0 syn gave a mixture (1:2) of ketone (121) and aldehyde (122). While a 4:5 mixture of the isomers 119 and 120 gave a 1:3 mixture of ketone (121) and aldehyde (122). The greater yield of ketone from isomer (119) with the S-0 and hydrogen syn is again due to the greater ease of hydrogen abstraction by the S-0.
Preparation and rearrangement of the cyclic sulphites of the substituted cyclohexane-1,2-diols (46-57, 60-63).

The unsubstituted, 1-methyl, 2-methyl and 1,2-dimethyl 4-tert-butylcyclohexane-1,2-diols were prepared. For each series four stereochemical diol isomers are possible. The nomenclature of the diols is such that the tert-butyl group is situated on the α-face of the cyclohexane ring. Thus the unsubstituted diol with both hydroxyls in equatorial positions (47) is named 4α-tert-butylcyclohexane-1β,2α-diol, and the dimethyl diol with the same stereochemistry (61) is named 4α-tert-butyl-1α,2β-dimethylcyclohexane-1β,2α-diol. The cyclic sulphites are named after the diols, with the further prefix A or B depending on whether the 3-0 points toward the α-face (A-isomer) or toward the β-face (B-isomer) of the molecule. Fig. 10 shows the cyclic sulphite isomers of the diol 47.

Preparation of the substituted cyclohexenones (31, 33, 42, 45).

The alkenes were prepared via 4-tert-butylcyclohexanone (29) and 4-tert-butyl-2-methylcyclohexanone (36) (Fig. 13). Ketone (29) was prepared by Jones oxidation of 4-tert-butylcyclohexanol (28, Koch-Light). The methyl-ketone (36) was initially prepared by methylation of the ketone (29).
Two procedures for the methylation of ketone(29) were investigated. The first involved introduction of an ethoxy-group adjacent to the carbonyl via the ethoxy-carbonyl ketone(34). Methylation followed by hydrolysis produced a mixture of starting ketone(29) and methyl ketone(36). Fractionation yielded pure methyl ketone(36). However the yield (ca. 10-15%) was far too low for this procedure to be useful as a synthetic route. The second procedure was a Stork methylation via an enamine; but again the yield of methyl ketone was too low (35-40%) for this route to be practicable.

The methyl ketone(36) was finally prepared in sufficient quantity by hydrogenation of 4-tert-butyl-o-cresol(39) to 4-tert-butyl-2-methylcyclohexanol(40), followed by Jones oxidation and distillation to give pure methyl ketone(36).

The unsubstituted alkene(31) and the 2-methyl alkene(42) were prepared by base (NaOMe) initiated decomposition of the benzene sulphonyl hydrazones(30,41) of the ketones(29,36). This reaction, known as the Rumford-Stevens reaction, was carried out under aprotic conditions, MeOH being distilled from the reaction mixture as it was formed. Under these conditions the reaction involves a carbene intermediate (Fig.11). The product from the 2-methyl ketone(36) was a 4:1 mixture of the 4-tert-butyl-2-methyl alkene(42) and
the 5-tert-butyl-3-methyl alkene (43).

Reaction of the two ketones (29 and 36) with MeMgI gave the 1-methyl and 1,2-dimethyl cyclohexanols (32, 44). The alcohols (32, 44) were dehydrated to the respective alkenes (33, 45) by heating with iodine to 140-150°. Dehydration of the dimethyl alcohol (44) produced a 4:1 mixture of the 4-tert-butyl-1,2-dimethyl alkene (45) and the 5-tert-butyl-2,3-dimethyl alkene (123). Both of the olefin forming elimination reactions proceed to give the more highly substituted alkenes as the major product, the reactions thus obeying Zaitsev's rule.

**Preparation of the substituted cyclohexane-1,2-diols (46-57, 60-63).**

The majority of the diols were prepared by oxidation of the appropriate alkene. The exceptions were the unsubstituted (47) and dimethyl (61)-diesquatorial diols. (Fig. 13).

Diol (47) was prepared by the sodium-isopropanol reduction of the keto-esters (65, 66). The product was a 4:1:1 mixture of the diesquatorial diol (47) and the two cis-isomers (48, 49). As the reduction (i, Fig. 12) proceeds, the equilibration between the reduced and non-reduced species (ii, Fig. 12) enables the thermodynamically more stable product to be formed.
The dimethyl disequatorial diol(61) was prepared by the reaction of the 1 - methyl ketol(67) with MeMgI.

The assignment of the stereochemistry to the diols was made initially on the basis of their mode of formation. The cis-diols were prepared by hydroxylation with KMnO₄ or iodine-silver acetate-H₂O and the trans-diols by hydroxylation with performic acid.

Permanganate oxidations when carried out in basic solutions, produce cis-diols via a cyclic manganese ester. Collapse of this ester then gives the products₄₂,₅₆(Fig.14). In the tert-butyl-cyclohexane system attack by the permanganate may occur on either face of the molecule and thus lead to two alternative permanganate esters(124,125). The preferred direction of attack will be governed by the steric constraints imposed, by the molecule, upon the entering KMnO₄.

Oxidation with iodine-silver acetate-H₂O also leads to cis-diols, however the diol stereochemistry is normally opposite to that obtained from a KMnO₄ oxidation.₄₄,₅₆. Iodine and silver acetate form a complex (Simonini Complex)₅₆ which reacts with the double bond to form an iodonium ion(126). Nucleophilic attack by acetate followed by acetate assisted expulsion of the iodine affords the acetonium ion(127). In the presence of water, hydrolysis of the acetonium ion occurs at the bridge-head carbon thus producing the cis-diol (Fig.15).
The initial addition of iodine will occur on the least hindered face and the subsequent reaction will lead to the cis-diol of stereochemistry opposite to that from KMnO₄ oxidation. In the absence of water nucleophilic attack on the acetonium in by acetate produces the trans-diacetate (Fig.15).

Oxidation of the alkenes with formic acid-hydrogen peroxide gave trans-diols. This trans-stereochemistry results from the formic acid catalysed ring opening of the epoxide⁵⁶,⁶³(Fig.16).

The assignment of stereochemistry to the trans-unsubstituted diols(⁴⁶,⁴⁷) was made on the basis of their mode of preparation, the diequatorial diol(⁴⁷) being formed from the sodium-isopropanol reduction and the diaxial diol(⁴⁶) formed from the opening of the epoxide. The assignments were confirmed by the NMR spectra of the two diols (Table 3), the protons geminal to the hydroxyls in the diaxial diol(⁴⁶) being at lower field and the signal less broadened than the protons in the diequatorial diol(⁴⁷). It is a feature of cyclohexane systems that signals from protons in an axial position tend to be broadened to a greater extent than the signals from equatorial protons.⁵⁹,⁶⁰. This is the result of the vicinal angles between the axial and equatorial protons, and adjacent protons to which they are coupled. This fact was used to assign the stereochemistry of each of the mono-methyl diols
(50-57; Table 3). Knowledge of the mode of preparation of the diol, in conjunction with the NMR was sufficient to define the stereochemistry in each case.

The stereochemistry of the cis-unsubstituted diols (48, 49) could not be defined by consideration of the NMR spectra (Table 3).

Table 3. NMR of protons and methyl groups seminal to the hydroxyl groups in diols 46-57.

<table>
<thead>
<tr>
<th>Diol</th>
<th>axial H</th>
<th>equatorial H</th>
<th>axial Methyl</th>
<th>equatorial methyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td></td>
<td>3.83(12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>3.50(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48, 49</td>
<td>3.57(18)</td>
<td>3.99(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>3.53(19)</td>
<td>3.69(7)</td>
<td>1.17</td>
<td>1.26</td>
</tr>
<tr>
<td>51</td>
<td>3.33(16)</td>
<td></td>
<td>1.22</td>
<td>1.25</td>
</tr>
<tr>
<td>52</td>
<td></td>
<td>3.67(7)</td>
<td>1.22</td>
<td>1.25</td>
</tr>
<tr>
<td>53</td>
<td>3.47(17)</td>
<td>3.50(6)</td>
<td></td>
<td>1.25</td>
</tr>
<tr>
<td>54</td>
<td></td>
<td>3.56(6)</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td></td>
<td></td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>3.28(20)</td>
<td></td>
<td></td>
<td>1.25</td>
</tr>
</tbody>
</table>
An attempt was made to assign the stereochemistry to these compounds by chemical means (Wolff-Kishner on the keto-benzoate 65) but these were unsuccessful. Tentative assignments* have been made on the basis of the epoxidation of the alkene(31). Epoxidation occurs preferentially$^57(60:40)$ on the $\alpha$-face and it is assumed that $\text{KMnO}_4$ will prefer to attack the same face. This tentative assignment is supported by the product ratios from the pyrolysis of the cyclic sulphites of these diols (discussed later).

The stereochemistry of each of the dimethyl diols(60-63) was assigned by comparing the physical data (IR, NMR, TLC, m.p.) of the diols from the oxidations, to the diols obtained from the reaction of MeMgI on the ketols 67 and 68. The stereochemistry of the ketols is known since the diols from which they are formed are of known stereochemistry. The NMR data of these ketols (Table 4) is consistent with the stereochemistry as shown (cf. Table 7), the methyl group at lower field occupying the axial position.

**Table 4.** Product ratios from the action of MeMgI on the ketols 67 and 68.

<table>
<thead>
<tr>
<th>Ketol (Me ppm)</th>
<th>Diol 60</th>
<th>Diol 61</th>
<th>Diol 62</th>
<th>Diol 63</th>
</tr>
</thead>
<tbody>
<tr>
<td>67 (1.37)</td>
<td></td>
<td>1</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>68 (1.23)</td>
<td>4</td>
<td></td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

* Diol 48 is the subject of an X-ray study to confirm these assignments.
The product ratios from the Grignard reactions can be rationalized by assuming the largest group is the solvated-OMg\textsuperscript{+} which hinders attack by the Grignard reagent on that side of the molecule.

The diol mixtures obtained from the reactions discussed were separated by column chromatography (5\% deactivated alumina) or by fractional crystallization from Et\textsubscript{2}O-pentane. The cis-2-methyl diols\textsuperscript{(56,57)} could not be separated by chromatography or crystallization. The diols were converted to their monoacetates\textsuperscript{(58,59)} which were separated by column chromatography and the diols obtained by subsequent hydrolysis. Purification of the diols was by crystallization from Et\textsubscript{2}O-pentane Table 5 summarizes the methods used to oxidize the alkenes and the ratios of isomers formed.

The performic acid oxidation of the symmetrically substituted alkenes\textsuperscript{(31,45)} produced only one product, the diaxial diols\textsuperscript{(46,60)}. However oxidation of either the 1-methyl-(33) or the 2-methyl-(42) alkene produces the two possible trans isomers. The dominating feature for the reactions of alkenes\textsuperscript{(31)} and \textsuperscript{(45)} is the preference for trans-diaxial opening of the epoxide intermediates. Trans-diaxial opening is preferred since only then can the departing oxygen and entering nucleophile maintain maximum overlap with the p-orbital. For the 1-methyl\textsuperscript{(33)} and 2-methyl
(42) epoxide intermediates there is still a preference for trans-diaxial opening.

**Table 5. Product ratios from the oxidation of the alkenes (31, 33, 42, 45).**

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Reaction</th>
<th>$%^a$</th>
<th>Stereochemistry</th>
<th>1&lt;sub&gt;α&lt;/sub&gt;, 2&lt;sub&gt;α&lt;/sub&gt;</th>
<th>1&lt;sub&gt;α&lt;/sub&gt;, 2&lt;sub&gt;β&lt;/sub&gt;</th>
<th>1&lt;sub&gt;β&lt;/sub&gt;, 2&lt;sub&gt;α&lt;/sub&gt;</th>
<th>1&lt;sub&gt;β&lt;/sub&gt;, 2&lt;sub&gt;β&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsub. (31)</td>
<td>KMnO₄</td>
<td>50</td>
<td></td>
<td>4</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂O₂−HCOOH</td>
<td>63</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-methyl (33)</td>
<td>KMnO₄</td>
<td>54</td>
<td></td>
<td>40</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>I₂−AgCH₃COO</td>
<td>55</td>
<td></td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methyl (42)</td>
<td>KMnO₄</td>
<td>50</td>
<td></td>
<td>1</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂O₂−HCOOH</td>
<td>45</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethyl (45)</td>
<td>KMnO₄</td>
<td>56</td>
<td></td>
<td>1</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂O₂−HCOOH</td>
<td>50</td>
<td>4</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>I₂−AgCH₃COO</td>
<td>58</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$a$ % Yield of diol product.

In highly acidic media nucleophilic attack on epoxides occurs preferentially at the tertiary center.⁵⁶ Performic oxidation of the 1-methyl alkene (33) will lead initially to two epoxide intermediates. In the trans-epoxide, nucleophilic
attack at the tertiary center will reinforce the preference for trans-diaxial epoxide opening. In the cis-epoxide nucleophilic attack at the tertiary center will oppose the preference for trans-diaxial cleavage and thus produce the trans-diequatorial diol(51). A similar argument can be applied to the epoxide intermediates from the 2-methyl alkene(42).

Oxidation of the unsubstituted alkene(31) with KMnO₄ leads predominantly to the α-configuration (Table 5). Assuming the reaction is under kinetic control this ratio of isomers (4:1) reflects an energy difference (at the transition state) between α- and β- hydroxylation of ca. 0.7 Kcals/mole. The ratio from the 1-methyl alkenes(40:1) indicates a preference for α- attack of ca. 2 Kcals/mole, while that from the 2-methyl alkene (1:4) a preference for β- attack of ca. 0.7 Kcals/mole. This reversal is rationalized in terms of a preference at the transition state for the methyl group to be pseudo equatorial.

At the transition state for α- attack on the 1-methyl alkene (128; Fig.17) the methyl group is moving toward an equatorial position, and for β-attack(129) it is moving toward an axial position. This effect reinforces the preference for α-attack, accounting for the 1.3 Kcals/mole difference in the transition states* (of unsubstituted alkene).

In the oxidation of the 2-methyl alkene(42) β-attack

* -Δ° methyl, equatorial-axial, is 1.7 Kcals/mole.
is favoured by the equatorial position of the methyl in the
transition state(131) and opposed by the preference for attack
at the least hindered face. A 4:1 ratio in favour of \( \beta \)-attack
is observed.

The dimethyl alkene(45) is attacked equally from the
\( \alpha \)- and \( \beta \)-face. Both the transition states contain a
pseudo-axial and equatorial methyl and on this basis neither
is favoured. Thus the product ratio expected would be the
same as that from the unsubstituted alkene. The observed
development is probably due to secondary steric factors.

The isomer distributions from the iodine-silver acetate
oxidation of the 1-methyl alkene(33) would seem anomalous in
that the major diol produced is the same as that predominating
from the K\( \text{MnO}_4 \) oxidation. Epoxidation of the alkene(33)
produces a small predominance(55:45)\(^{43}\) of the cis-epoxide,
thus the iodonium ions(132,133;Fig.18) should be formed in
approximately equal amounts and the diol products should be
the same. The diastereal acyl hypoiodite intermediates(134,136)
will be predominant ones formed from the iodonium ions.
Equilibration between these acyl hypoiodites, iodonium ions
and the alkene produces a situation where the stereochemistry
predominating will depend on the relative rates of formation
of the acetonium ions(138,139) from the intermediates(134,136).

The transition state in the step 134 \( \rightarrow \) 138(Fig.18)
involves a methyl in a pseudo-axial position and will be less favoured than the transition state in the step 136 → 139 where the methyl group remains equatorial. The intermediates 135 and 137 will react more slowly than 134 and 136 since in the former pair the molecule must adopt the boat conformation.

Preparation of the cyclic sulphites of the cyclohexane-1,2-diols.

The cyclic sulphites of the diols were prepared by reacting the diol with SOCl₂ in CH₂Cl₂. The sulphites were isolated by extraction with pentane and the isomers of the cis-diols were separated, but this was not achieved for the trans-diols. Chromatography of the cyclic sulphite isomers of the 1-methyl trans-diol(51) afforded mixtures of the two isomers ranging from 3:1 to 1:3. The assignment of stereochemistry about the sulphur atom was made on the basis of the NMR spectra, using the marked deshielding effect of the syn S-O bond which has been discussed above. The ratio of isomers A:B tended to vary depending on the procedure adopted in the preparation. The reactions were more stereospecific when carried out at room temperature or below(0°). Table 6 gives the NMR data for the cyclic sulphites.

Very little can be extracted from the NMR data for the unsubstituted diol-(47-49) cyclic sulphites. The A- and B-isomers of the cis-diols(48,49) can be distinguished by the
downfield shift of the protons when the S-O is syn. The
isomers for the trans-diol(47) cannot be distinguished since
both have an upfield and downfield proton.

Comparison of the methyl resonances for the cyclic sulphite
isomers of the diol pairs 51/55, 52/57 and 53/56 indicates
that there is little or no distortion of the cyclohexane ring
from the chair conformation e.g. in the cis-diol(52,57) cyclic
sulphites the methyl groups are at 1.66 and 1.70 when the S-O
is syn, and at 1.38 and 1.40 when the S-O is anti.

In the cis-diol cyclic sulphites the equatorial position
is more strongly affected by the orientation of the S-O, than
the axial position. The situation is shown in diagram 140.

It is evident from the diagram(140) that the equatorial
group (R[e]) is closer to, and more aligned with the S-O bond than
is the axial group (R[a]). This causes the equatorial group in
these cis-compounds to be more strongly affected by the S-O
orientation.

Finally in changing the orientation of the S-O, the change
in the resonance of the axial methyls in the trans-sulphites,
parallels the change of the equatorial methyls in the cis-
sulphites. This is due to the axial methyl of the trans-
sulphites occupying the same relative position to the S-O(141)
as did the equatorial methyl of the cis(140).
Table 6. Proton and methyl group NMR data for the
cyclohexane diol cyclic sulphonates.

<table>
<thead>
<tr>
<th>Diol</th>
<th>A-isomer</th>
<th>B-isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R₁ ppm</td>
<td>R₂</td>
</tr>
<tr>
<td>Unsubstit.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>4.17</td>
<td>3.67</td>
</tr>
<tr>
<td>48</td>
<td></td>
<td>4.53</td>
</tr>
<tr>
<td>49</td>
<td></td>
<td>5.00</td>
</tr>
<tr>
<td>1-methyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>1.53(ax)</td>
<td>3.83(ax)</td>
</tr>
<tr>
<td>52</td>
<td>1.38(eq)</td>
<td>4.30(ax)</td>
</tr>
<tr>
<td>53</td>
<td>1.55(ax)</td>
<td>4.77(eq)</td>
</tr>
<tr>
<td>2-methyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>4.38(ax)</td>
<td>1.25(ax)</td>
</tr>
<tr>
<td>56</td>
<td>4.20(eq)</td>
<td>1.45(ax)</td>
</tr>
<tr>
<td>57</td>
<td>4.73(ax)</td>
<td>1.70(eq)</td>
</tr>
<tr>
<td>Dimethyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>62 63</td>
<td>1.58(eq)</td>
<td>1.48(ax)</td>
</tr>
<tr>
<td>63 62</td>
<td>1.40(ax)</td>
<td>1.23(eq)</td>
</tr>
</tbody>
</table>
Identification of the pyrolysis products (73-82; 29:142).

The 3-tert-butyl ketone (142) was a commercial sample (Koch-Light) and the preparation of the 4-tert-butyl ketone (29) has already been discussed. The methyl ketones (73-76) were obtained by CrO₃-pyridine oxidation of the alcohols (69-72). These alcohols were prepared by hydroboration of the respective alkenes followed by oxidation with alkaline peroxide. The stereochemistry of the hydroxyl group was established from the NMR spectra of the geminal proton, and the knowledge that hydroboration is a cis-addition. The products obtained from the hydroboration (1:1 Table 7) reflect the preference for the methyl group to occupy an equatorial position. The NMR spectra of isomers 69 and 72 (Table 7) is unusual in that the methyl groups appear as broadened singlets. This can only be due to the methyl and the geminal proton having the same chemical shift.

Alcohols (69) and (70) were separated by column chromatography (alumina) and oxidized to the respective ketones (73, 74). Alcohols (71) and (72) were not separable by column chromatography and the mixture (3:1) was oxidized to the ketones (75, 76). The major product was assigned stereochemistry (76) by NMR comparison with (73) and (74) (Table 7), and since the major product (72) in the alcohol mixture had an equatorial methyl.
The dimethyl ketones (77,78) were prepared by methylation of the methyl ketones (73-76) with MeI and NaNH₂ in Et₂O.

The NMR data for the ketones shows the axial methyl groups at lower field than the equatorial methyl groups. This is the opposite to the situation observed in the 1- and 2- methyl diols (50-57; Table 3), and the alcohols (69-71; Table 7). The equatorial methyl is shifted to higher field by the diamagnetic anisotropy shielding of the carbonyl group. ⁵⁹,⁶⁰

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>ratio</th>
<th>ppm(Wh/2 or 3)</th>
<th>H</th>
<th>Me</th>
<th>Ketone</th>
<th>Me</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.05(2.5)</td>
<td>1.03(J,6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-methyl</td>
<td>69</td>
<td>3</td>
<td>3.06(17)</td>
<td>0,16(J,7)</td>
<td>73</td>
<td>1.15(J,7)</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>1</td>
<td>3.68(7)</td>
<td>0,16(J,7)</td>
<td>74</td>
<td>1.15(J,7)</td>
</tr>
<tr>
<td>2-methyl</td>
<td>72</td>
<td>3</td>
<td>3.07(16)</td>
<td>1.03(J,6)</td>
<td>76</td>
<td>1.02(J,6)</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>1</td>
<td>3.80(6)</td>
<td>0.93(J,7)</td>
<td>75</td>
<td>1.15(J,7)</td>
</tr>
<tr>
<td>Dimethyl</td>
<td>77</td>
<td>1.15, 1.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>1.13, 1.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Product ratio from the hydroboration of the alkene.
The cyclopentane pyrolysis products(79-82) were identified by their physical data (IR, NMR, mass spec.) after isolation from the product mixture by preparative GLC. These products are isomeric(143,144), but where the two possible isomers were isolated(80) and (82) they could not be distinguished by GLC or NMR. The aldehyde(79) should consist of a mixture of the two isomers but they could not be distinguished experimentally.

Rearrangement of the cyclohexane-diol cyclic sulphites.

The cyclic sulphites were pyrolysed by heating to 250°-280° under a stream of nitrogen until SO₂ was no longer evolved. The products were either identified by GLC comparison with authentic samples prepared independently or isolated by preparative GLC and identified in the normal manner.

A mixture of the 2-methyl ketones(73,74) was heated to 250° for 20 minutes under a stream of SO₂. GLC analysis of the mixture showed that the ratio had changed from 7:3 to 9:1. Thus it is possible for the methyl ketones(73-76) to equilibrate under the pyrolysis conditions.

The results obtained are shown in Tables 8,9. The product ratios for the 1-methyl-disquatorial diol(51) cyclic sulphites were obtained by extrapolation of the results from 1:3, 1:1 and 3:1 ratios of the two isomers. The sulphite isomers of the 2-methyl-disquatorial diol(55) could not be separated and the product ratio shown is for a 1:1 mixture of
the A- and B- isomers. For the methyl ketones(73-76) the ratio of equatorial to axial methyl varied from 3:1 to 6:1.

All of the products can arise from 1,2-migrations of hydride, methylene or methyl(Fig.19). The stereoelectronic requirement for carbonium ion rearrangements is assumed to be operative i.e. the groups involved in the migration must be trans and coplanar. This restricts the favourable migrations available to the molecule in any given conformation.

The conformations available to a tert-butyl cyclohexane system, with approximate energy differences (kcal/mol)\(^1,58\) are shown in Fig.20. It has been assumed the difference between the chair and the boat conformations are the same as in cyclohexane, and that a tert-butyl group favours an equatorial position by 5 kcal/mol. The population figures were obtained by using the energy values in the equation \(\log_e n = -E/RT\). When conformation (i) has an equatorial methyl the energy values are decreased by 1.7, and conversely when i has an axial methyl.

In the 4-tert-butylcyclohexane cyclic sulphite system under study, the cis-isomers are conformationally more mobile than the trans-isomers. Conformations ii, iii and vi are not available to the trans-isomers(Fig.21).

Rearrangement of the unsubstituted and dimethyl compounds may occur by cleavage of either the Cl-O or the C2-O bond, while in the methyl isomers preferential cleavage of the tertiary C-O bond occurs.
<table>
<thead>
<tr>
<th>Diol</th>
<th>Cyclic sulphite isomer</th>
<th>3-t-butyl ketone (142)</th>
<th>4-t-butyl ketone (29)</th>
<th>Cyclopentane aldehyde (79)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsub.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>A and B</td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>48</td>
<td>A and B</td>
<td>73</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>A and B</td>
<td>23</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>Dimethyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>A and B</td>
<td>3</td>
<td>19</td>
<td>78</td>
</tr>
<tr>
<td>63</td>
<td>A and B</td>
<td>16</td>
<td>8</td>
<td>76</td>
</tr>
</tbody>
</table>

The products (Table 8) from the cis-unsubstituted cyclic sulphites arise from cleavage of axial C-O bonds, with accompanying hydride migration. Cleavage of the equatorial C-O bond, with hydride migration, must occur in the boat conformation (Fig. 20) since only then are the groups trans-coplanar. The lower activation energy of the reaction from the boat conformation is due to the relief of steric strain in the transition state. The trans-unsubstituted isomer is conformationally fixed and rearranges by cleavage of an equatorial C-O bond with accompanying methylene migration.
The cis-dimethyl isomers pyrolyse (Table 8) with preferential cleavage of an equatorial C=O bond and methylene migration, rather than cleavage of the axial C=O bond and migration of the axial methyl group. The methyl migration is hindered by the cis-equatorial methyl in both the chair and boat conformations (145,146).

The stereochemistry about the sulphur atom has no effect on the product ratios obtained from the unsubstituted and dimethyl series, in contrast to the marked effect it has on the product ratios from the 1- and 2-methyl series (Table 9). The effect is similar to that already observed in the pyrolysis of the hydrobenzoin cyclic sulphites i.e. abstraction of a proton by the syn S=O to form the enol of a ketone. This mechanism is substantiated by the fact that much more ketone is observed from those compounds that have the S=O and proton syn, and that no effect is observed in the dimethyl series where no such mechanistic pathway is available.
Table 9. Results from the pyrolyses of the 1-methyl and 2-methyl diol cyclic sulphites.

<table>
<thead>
<tr>
<th></th>
<th>1-methyl</th>
<th>methyl ketones (75,76)</th>
<th>cyclopentane aldehyde (80)</th>
<th>cyclopentane ketone (81)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>25</td>
<td>70</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>72</td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td>52</td>
<td>A and B</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>A</td>
<td>89</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>63</td>
<td>37</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>2-methyl</th>
<th>methyl ketones (73,74)</th>
<th>aldehyde (80)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>A:B, 1:1</td>
<td>41</td>
<td>59</td>
</tr>
<tr>
<td>55</td>
<td>A</td>
<td>53</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>57</td>
<td>A and B</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

a) The products ratios for these isomers were calculated by extrapolating the results obtained from the pyrolysis of 1:3, 1:1 and 3:1 mixtures of 51A:51B.

The 1-methyl diol cyclic sulphites pyrolyse to give the ketones (75,76,81) and aldehyde (80) (Table 9). The methyl ketones (75,76) are the major products from the cis-isomers and the trans isomer when the S-O and hydrogen are syn (51B).
The formation of the methyl ketone(81) from the trans-diol(51) sulphites occurs by cleavage of the secondary C-O bond and accompanying methylene migration. Since no similar product was observed from the pyrolysis of the 2-methyl-trans diol(55) sulphites (Table 9), its formation must be due to steric effects peculiar to the trans-1-methyl sulphites(51A,51B).

The 2-methyl diol cyclic sulphites pyrolyse to give the methyl ketones(73,74) and cyclopentane aldehyde(81). The trans-2-methyl sulphite isomers were not separable and a 1:1 mixture was pyrolysed. The effect of the S-O stereochemistry is again demonstrated by the results from the isomers(56A) and (56B) (Table 9).

Pyrolysis of the cis-sulphites with an equatorial methyl group(52A,B; 57A,B), produced ketones as the sole product (Table 9) by way of a hydride migration. The aldehydes can only be formed while the molecule is in the boat conformation (ii; Fig.20) which is less favoured for these compounds, since it involves a methyl moving from an equatorial to an axial position. Aldehyde formation also requires a methylene migration which is likely to be slower than the hydride migration occurring in the favoured conformation. In contrast the cis sulphites with an axial methyl substituent(53A,B;56A,B) gave mixtures of methyl ketones(73-76) and aldehyde(80), ketone being the major product regardless of the S-O stereochemistry (Table 9). The predominance of the ketone
product from the isomer where the S-O and H are anti(53E, 56A; Table 9) is due to a rapid hydride migration occurring in the boat conformation, which is more readily accessible since it involves an axial methyl moving to an equatorial position (Fig. 20).

The pyrolysis of the trans-diol(51, 55) cyclic sulphites produced mixtures of methyl ketones(73-76) and aldehyde(80). Aldehyde was the major product from that isomer where the S-O and H are anti(51A; Table 9). This is in contrast to the cis-isomers(53B, 56A; Table 9) above and reflects the much greater rigidity of the trans-diss-equatorial cyclic sulphite system. Ketone formation from the trans-isomer(51A) (S-O/H anti) is by way of a cis 1,2-hydride shift which implies a considerable degree of charge separation in the transition state.

Of the mechanistic pathways outlined in the Introduction, 'a' and 'b' are operative. Pathway 'c' requires migration to a carbonium ion separated from its anion in which cis-migration may occur as readily as trans. cis-Migration is observed only in the pyrolysis of the trans-sulphite(51A) discussed above. If a carbonium ion is the intermediate then sulphites (51A) and (52A)(Fig. 22) should pyrolyse to give similar product ratios, since the reactions would proceed via the same intermediate (147; Fig. 22). This is not what is observed(Fig. 22).

The cyclic sulphites pyrolyse by preferential cleavage of
a tertiary carbon-oxygen bond, and rearrange via a hydride shift provided an appropriate conformation is available.
APPENDIX A.

The mechanism of 1,3-dioxolane formation from the BF$_3$-catalysed reaction of epoxides with carbonyl compounds.

Yandovskii and Temnikova$^{61}$ recently postulated a mechanism for the formation of 1,3-dioxolanes from epoxides and carbonyl compounds under Lewis acid conditions (Fig.23). This mechanism is now supported for the BF$_3$-catalysed reaction of but-2-ene and cyclohexene epoxides with acetone.

The experiments exclude the possibility of the alternate mechanisms (ii) and (iii) (Fig.24). Mechanism (ii) required the presence of a sufficient concentration of water impurity to produce the diol(109) as an intermediate which would subsequently react with carbonyl compound to produce dioxolane and regenerate water.

Reaction of either cis-but-2-ene epoxide(106) or di,1-butane-2,3-diol(109) with acetone in the presence of BF$_3$-etherate gave the trans-dioxolane(115). Similar treatment of either trans-but-2-ene epoxide(107) or meso-butane-2,3-diol(108) gave the cis-dioxolane(114). The diols(108,109) reacted to produce the expected dioxolane, but the correct interpretation of the inversion accompanying dioxolane formation from the epoxides was not clear. However, mechanism (iii) may be excluded since it would lead either to retention of configuration,
or more probably to mixtures of cis- and trans-dioxolanes from each epoxide.

Similarly reaction of cyclohexene epoxide with acetone in the presence of BF$_3$-etherate produced the trans-dioxolane(112) exclusively (Fig. 25) by mechanism (i) or (ii) since (iii) would lead to the cis-dioxolane(113) or a mixture of the two.

In an attempt to decide which mechanism (i) or (ii) was operating the butane diol and but-2-ene epoxide reactions were repeated using O$^{18}$-labelled acetone (8.9% enriched). Mass spectra for the products and the O$^{18}$-enriched acetone were recorded at 17eV on a MS902 instrument at a resolving power of 1000 without changing either the source or detector settings. No O$^{18}$-incorporation in the dioxolanes was detected for the diol reactions (as expected), but almost quantitative incorporation was found for the epoxide reactions (Table 10). This result would seem to exclude mechanism (ii), however the free water postulated in the system would be recycled and itself become O$^{18}$-labelled; the O$^{18}$ content of the dioxolane product would be reduced, for low water concentrations (up to ca 0.3 mole), by at least the ratio mole H$_2$O/moles epoxide. In order to exclude this possibility the epoxide O$^{18}$-labelled acetone reactions were repeated in the presence of added water (0.2 moles). If mechanism (ii) were operating the maximum O$^{18}$ content which could be found for the dioxolane
product would be 80%. Since $^{18}_0$-incorporation was unchanged by addition of water, mechanism (ii) may be excluded. Mechanism (i) remains for the $\text{BF}_3$-catalysed formation of dioxolanes from but-2-ene epoxides and acetone, and very probably, the $\text{BF}_3$-catalysed formation of dioxolanes from cyclohexene epoxide and acetone.

Table 10. Percentage of possible theoretical $^{18}_0$-incorporation ($\pm 3\%$) in 2,2,4,5-tetramethyl-1,3-dioxolane from reaction of $^{18}_0$-acetone (8.96% moles) with substrate (1 mole).

<table>
<thead>
<tr>
<th></th>
<th>No H$_2$O added</th>
<th>0.2 moles H$_2$O added</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-But-2-ene epoxide (106)</td>
<td>99.4</td>
<td>96.8</td>
</tr>
<tr>
<td>trans-But-2-ene epoxide (107)</td>
<td>97.8</td>
<td>102</td>
</tr>
<tr>
<td>d,1-butane diol (109)</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>meso-butane diol (108)</td>
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</tbody>
</table>
APPENDIX B.

Mass spectra of the cyclohexane-1, 2-diols.

There has been considerable interest in the mass spectra of alicyclic vicinal glycols,\textsuperscript{64,65} and the influence of stereochemistry on the fragmentation patterns of alcohols.\textsuperscript{66,67,68}

The mass spectra of the four series of cyclohexane-1,2-diols were examined in an attempt to uncover any systematic effect of the stereochemistry on the fragmentation pattern. Stereochemical effects should be most apparent in the spectra obtained at 12eV (Fig.29-31), and from examination of the 12eV spectra three features were apparent.

(a) The difference between the unsubstituted diols.
(b) Lack of difference in the substituted diols.
(c) The marked effect in shifting the methyl group from the 1- to the 2- position.

The postulated fragmentation patterns for the substituted diols (Fig.26-28) involve cleavage of the cyclohexane ring as the initial step. The methyl group is assumed to stabilize the charge on the hydroxyl geminal to it, leading to the cleavage direction shown (Fig.26-28). Cleavage of the ring eliminates the stereochemical difference and all four diols of a series will have the same fragmentation precursor.
Loss of the tert-butyl group produces the ion at m/e 129, and differences in the 1-methyl and 2-methyl spectra arise from the relative stabilities of these ions.

The species at m/e 129 from the 2-methyl-diols has more paths available for stabilization, and fewer competing single step rearrangements leading to fragmentation than does the 129 ion from the 1-methyl diols. Thus the m/e 129 intensity is greater for the 2-methyl diols, the other peaks being correspondingly reduced (Fig.26-27; Fig.31).

The relative intensities of the peaks, in the spectra of the dimethyl diols, lie between those of the 1-methyl and 2-methyl diols (Fig.31). Two species at m/e 143 will be initially formed presumably in equal amounts, but one will fragment more rapidly than the other. Ion 143b (Fig.28) will lead to a fragmentation pattern similar to the 1-methyl series while ion 143a (Fig.28) will lead to a pattern similar to the 2-methyl series. Examination of the $m^+_{+} / H_2O / m^+_{+}$ ratios (Table 11) for the substituted diols reveals no dependence on stereochemistry, providing further confirmation of the open ring nature of the initial ion at m/e 186.

For the unsubstituted diols the situation is more complex (Fig.29,30). Accurate mass measurement reveals five fragmentation processes occurring from the molecular ion. These are loss of water, and loss of 57,56,55 as
C₄H₉ or C₃H₆O, C₄H₈ and C₄H₇ respectively. The losses can occur either from an open chain parent or from a parent where the relative stereochemistry of the diol is maintained. The latter must be the case for many of the fragmentation processes e.g. the loss of 18(H₂O) and 55(C₄H₇).

Loss of water from cyclohexanols occurs largely by 1,3-or 1,4-abstractions, abstraction of a tertiary hydrogen being preferred. It has been found that for an extensive series of tert-butylocyclohexanols elimination of water occurs most readily from the trans-isomer. In 4-tert-butyl cyclohexanol the process occurs via a 1,4-abstraction in the boat conformation, and in 3-tert-butylocyclohexanol by a 1,3-trans-diaxial process (i and ii, Fig. 32).

In the unsubstituted diols the greatest loss of water occurs from diol(49) where both hydroxyl groups are positioned to undergo the most favourable abstraction of a hydrogen (iii, Fig. 32). This is reflected in the overall pattern by the base peak at m/e 80, which arises by the loss of two molecules of water and the tert-butyl group.

Loss of 55(C₄H₇) only occurs to a significant extent from that diol(48) where the stereochemistry allows the tert-butyl and the hydroxyl groups to be in close proximity in a boat conformation.
Table 11. Loss of water from the M⁺ ion of the cyclohexane-1,2-diol.

<table>
<thead>
<tr>
<th>Stereochem.</th>
<th>1,2</th>
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</thead>
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<tr>
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<td>0.05</td>
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<td>M⁺</td>
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</tr>
<tr>
<td>1-Me.</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>M⁺⁻H₂O</td>
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<tr>
<td>M⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Me.</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>M⁺⁻H₂O</td>
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<td>0.04</td>
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<tr>
<td>M⁺</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Di-Me</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>M⁺⁻H₂O</td>
<td>2.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>M⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
EXPERIMENTAL

Melting points are uncorrected. Infra-red spectra were recorded on a Shimadzu IR-27G Spectrometer for liquid films and nujol mulls. NMR spectra were recorded for 10% w/v CDCl₃ solutions, with TMS and CHCl₃ as internal standards, on a Varian A60 spectrometer with a Varian Model V-6058A spin decoupler. NMR spectra for other solvents and other concentrations are indicated. Analytical GLCs were recorded on a Varian Aerograph 1200 with a flame ionization detector. The columns used were 3m 3% SE30 on Chromosorb G, 3m 2% Carbowax 20M on Chromosorb G, 2m 2% Carbowax 4000 on Chromosorb G and 7m 2% PEGA on Aeropak 30. Preparative GLCs were carried out on an Aerograph Autoprep 705 with a flame ionization detector. The columns used for preparative GLC were 3m 10% SE30 on Chromosorb W or 4m 7% FFAP on Chromosorb W. Elemental micro-analyses were determined at the University of Otago. Mass spectra were recorded on an AEI Model M3 902 spectrometer. Spinning band distillations were done on a Heeter-Faust 8mm Annular Teflon spinning band.

The alumina used for column chromatography was P. Spence Grade II 5% or 10% deactivated, prepared by addition of 5% v/v or 10% v/v of 10% aqueous HAc respectively.
The silica gel used for column chromatography was Crosfield quality grade B.S.S. Sorbsil. All solvents for column chromatography were technical grade. Benzene was distilled of P2O5.

Merck silica gel G with binder and Fluka alumina type H were used for TLC. The alumina plates were deactivated by being left open to the atmosphere for 2-3 days. Benzene, CHCl3 and CHCl3-acetone mixtures were the solvents most commonly used for developing the chromatograms. The visualizing agents used were iodine or phosphomolybdic acid in EtOH.

4-tert-Butylcyclohexanone(29)

4-tert-Butylcyclohexanol(28,100g) was dissolved in acetone(250ml) and Jones Reagent (CrO3,10.3:H2SO4,3.7:H2O,30) was added dropwise until the reaction mixture remained a brown colour. After stirring for a further 30 minutes the reaction mixture was worked up by the addition of Na2SO3(aq.) until a permanent green colour resulted. The product was isolated by extraction with Et2O. Distillation afforded GLC pure (Carbowax 20M) 4-tert-butylcyclohexanone(29,85g,80%) m 48-50°(Lit.34 49-50°); ν max 1715, 1220, 1165, 945cm⁻¹; NMR δ 0.93(8,9H; tert-butyl); 1.5-3.4ppm(methylene groups).
4-tert-Butylcyclohexyl benzene sulphonyl hydrazone (30).

To a solution of benzene sulphonyl hydrazone (98g) in acetic acid (100ml) was added 4-tert-butylcyclohexanone (75g) in acetic acid (100ml). After stirring one hour the reaction mixture was diluted with water and the product collected by filtration. 4-tert-Butylcyclohexyl benzene sulphonyl hydrazone (30, 120g, 80%) \( \nu \) max 3500, 1630, 1158, 1090 cm\(^{-1}\).

4-tert-Butylcyclohexene (31).

A suspension of NaOMe (100g) in diglyme (1500ml) in a 3-necked flask (3000ml) fitted with stirrer and distillation head, was heated to 150-155\(^{\circ}\). 4-tert-Butylcyclohexyl benzene sulphonyl hydrazone (30, 120g) was added at such a rate to keep the temperature of the distillate below 80\(^{\circ}\). When the addition of hydrazone was complete the reaction mixture was stirred for one hour at 150\(^{\circ}\)-155\(^{\circ}\). After cooling, the combined distillate and reaction mixture was extracted with pentane. Removal of the solvent and distillation afforded GLC pure (Carbowax 4000) 4-tert-butylcyclohexene (31, 35g, 55%)

\( \beta_{20} \) 62-63\(^{\circ}\) (Lit\(^{35}\) \( \beta_{10} \) 53\(^{\circ}\)-54\(^{\circ}\)); \( \nu \) max 1660, 1470, 1355, 1120, 670 cm\(^{-1}\); NMR \( \delta \) 5.66 (\( \text{NH} / 2 \) 5Hz, 2H; C=CH\(_2\)); 0.98 (8, 9H; tert-butyl); 1.0-2.5 ppm (methylene groups).

4-tert-Butyl-1-methylcyclohexanol (32). \(^{36}\)

To a solution of MeMgI (1.3 moles) in Et\(_2\)O was added 4-tert-butylcyclohexanone (1 mole) dropwise with vigorous
stirring. When the addition was complete the reaction mixture was heated under reflux for one hour then hydrolysed by the addition of NH₄Cl(aq.). The product was isolated by extraction with Et₂O and consisted (GLC, Carbowax20M) of a mixture (1:1) of cis- and trans-4-tert-butyl-1-methylcyclohexanol (32, 0.9 moles, 90%) m. 53°-57°; v max 3340, 1190, 1135 cm⁻¹; NMR δ 2.2 (1H; 0-CH₃); 1.20 (s, 3H; COH-CH₃); 0.85 (s, 9H; tert-butyl); 0.8-1.9 ppm (methylene groups).

4-tert-Butyl-1-methylcyclohexene(33).

4-tert-Butyl-1-methylcyclohexanol(74g) was heated to 140° with iodine(0.5g) until one mole of water was distilled over. After cooling the reaction mixture was poured into Et₂O, washed with NaHSO₃ (aq.) and water, then dried (Na₂SO₄). Removal of the solvent and distillation yielded

4-tert-Butyl-1-methylcyclohexene (33, 45g, 70%)

b₂₀ 84°-86° (lit. 37b₁₁ 74°-75°); v max 1600, 1560, 1340, 1170, 905 cm⁻¹; NMR δ 5.33 (wh/2 7Hz; 1H; C=C-CH₃); 1.62

(s, wh/2 4Hz, 3H; C=C-CH₃); 0.87 (s, 9H; tert-butyl); 0.9-2.0 ppm (methylene groups).

Methylation of 4-tert-Butylcyclohexanone(29). 38, 39.

(a) 38 To a stirred solution of ketone(29, 49.5g) in diethyl oxalate(47g) at 30° to 40° was added sodium(7.4g) in EtOH(100ml). After standing 12 hours the reaction
mixture was poured into a mixture of ice(75g), H₂SO₄(conc.9ml) and diluted with water(750ml). The product was then extracted into Et₂O, washed with water and dried(Na₂SO₄). The Et₂O was removed and the residue heated to 180° for 12 hours with glass powder(10g) and a spatula of iron powder. Distillation gave 4-tert-butyl-2-ethoxy-cyclohexanone (34.28g) b₁₂ 140°-150°; ν max 1740, 1720, 1650, 1210cm⁻¹; NMR δ 4.20 (q, J7Hz, 2H:-OCH₂CH₃); 1.30(t, J7Hz, 3H:-OCH₂CH₃); 0.92(s, 9H; tert-butyl); 1.2-2.5 ppm(methylene groups).

To a solution of 4-tert-butyl-2-ethoxy-cyclohexanone (34.28g) and MeI(19.6g) in EtOH(20ml) was added sodium(2.9g) in EtOH(100ml) the temperature being maintained at 30°. When the addition was complete the reaction mixture was stirred in a cold room(4°) for 12 hours. After refluxing one hour, EtOH was removed by distillation and the residue diluted with water(500ml). 4-tert-Butyl-2-ethoxy-2-methylcyclohexanone(35,29g) was isolated by extraction with Et₂O.

The ester(35,29g) was heated under reflux in a solution of H₂SO₄(130ml, 30%) in AcOH(260ml) for 24 hours. After neutralization the product was isolated by extraction into Et₂O. Removal of the solvent and distillation afforded material(13g) consisting of a mixture(3:1) of methyl ketone(36)
and starting ketone(29). Distillation on a spinning band fractionation column gave GLC pure (Carbowax 20M) methyl ketone(36) consisting of a mixture(4:1) of the 2 -methyl and 2 -methyl isomers. 4-tert-Butyl-2-methylcyclohexanone (36,6g,15%) b\textsubscript{15} 96°-97°; \nu \text{max} 1715, 1220, 1150 cm\textsuperscript{-1}; NMR δ 1.15(d, J=7Hz; 2-CH\textsubscript{3}); 1.02(d, J=7Hz; 2x-CH\textsubscript{3}); 0.90(s,9H; tert-butyl); 1.3-2.6 ppm(methylene groups).

(b)\textsuperscript{39} 4-tert-Butylcyclohexanone(20g) was heated under reflux with cyclohexylamine(15.2g) in benzene(50ml) using a Dean-Stark apparatus to collect the water azeotroped from the reaction mixture. When separation of water stopped taking place (5 hours) benzene and excess cyclohexylamine were removed by distillation. The enamine(37) was added dropwise to Et\textsubscript{3}MgBr(1.1 molar xs) in dry THF(40ml). When the addition was complete the reaction mixture was heated under reflux for 4 hours. After cooling MeI(40g) was added and the reaction mixture heated under reflux until the pH was 9-10. The reaction mixture was then heated under reflux with HCl(400ml, 15%) for 3 hours. The product was isolated by extraction with Et\textsubscript{2}O. After distillation the product was fractionated through a spinning band to yield 4-tert-butyl-2-methylcyclohexanone(36,8g,35%) a 5:1 mixture of the two isomers.
4-tert-Butyl-o-cresol (39).

Freshly distilled o-cresol (420 g) was heated with phosphoric acid (100%, 1600 g) and tert-butanol to 60°-65° for 20 hours. The product was isolated by means of Et₂O. Fractionation through a 25 cm column packed with single turn glass helices yielded GLC pure (85%) 4-tert-butyl-o-cresol (39, 360 g, 70%) b₂₀ 125-128 (Lit. 740° 235-237); v max 3400, 1610, 1125, 1160, 320 cm⁻¹; NMR: 6 5.5-7.2 (4H, aromatic); 5.17 (1H; Ar-Oh); 2.20 (s, 3H; Ar-C₆H₃); 1.25 ppm (s, 9H; tert-butyl).

4-tert-Butyl-2-methyl-cyclohexanol (40).

The hydrogenations were carried out in a Chas. W. Cook and Son shaking autoclave fitted with a glass liner. 4-tert-Butyl-o-cresol (50 g) in EtOH (70 ml) was heated to 180° under 2500 psi of hydrogen, in the presence of Raney Nickel⁴¹ catalyst (6 g), for 10 hours. After cooling the product was poured into pentane and washed several times with NaOH (20%). Removal of the solvent yielded a mixture of the four isomers of 4-tert-butyl-2-methylcyclohexanol (40, 40 g, 80%); v max 3350, 1220, 1035, 980 cm⁻¹; NMR: 3.72 (1H; CH-OH); 2.0 (1H; O-H); 1.0 (q, 3H; CH₂-CH₃); 0.83 (s, 9H; tert-butyl); 0.8-2.2 ppm (methylene groups).
4-tert-Butyl-2-methylcyclohexanone (36).

The alcohol (40) was oxidized to the methyl ketone (36) by the Jones oxidation procedure described previously. Distillation afforded the ketone (36, 80%) as a mixture of the two isomers, pure by GLC (Carbowax 20M).

4-tert-Butyl-2-methylcyclohexylbenzene sulphonyl hydrazone (41).

The methyl ketone (36, 150g), benzene sulphonyl hydrazine (230g) and p-tolyl sulphonic acid (0.1g) were dissolved in MeOH and stirred at room temperature for one hour. On cooling to 4°C the product crystallized from the reaction mixture and was collected by filtration. 4-tert-Butyl-2-methylcyclohexyl benzene sulphonyl hydrazone (41, 280g, 80%)

\[ \nu_{\text{max}} 3500, 1625, 1170, 1085 \text{ cm}^{-1}. \]

4-tert-Butyl-2-methylcyclohexene (42).

The hydrazone (41, 280g) was decomposed with base in diglyme by the same procedure used to decompose the unsubstituted hydrazone (30). Extraction and distillation yielded product (117g) consisting of a mixture (4:1 by GLC, Carbowax 4000) of product (42) and 5-tert-butyl-3-methylcyclohexene (43) NMR: 5.60 (NH/2 10Hz, 2H; C=C-H), 0.97 (d, J=6Hz; CH\(_2\)), 0.88 (s, 9H; tert-butyl); 0.9-2.0 ppm
(methylene groups). Fractionation through a spinning band yielded GLC pure (carbowax 4000) 4-tert-butyl-2-methylocyclohexene (42, 54%, 50%) v\textsubscript{max} 720-740, 1450, 1055, 920 cm\textsuperscript{-1};

NMR \delta 5.40 (\textit{t}, 2 Hz, 1H; C=C-H); 1.67 (e, Wh/2 5Hz; C=C-C\textsubscript{2}H\textsubscript{5})

0.87(s, 9H; tert-butyl); 0.9-2.1 ppm (methylene groups).

4-tert-Butyl-1,2-dimethylocyclohexanol (44).

Methyl ketone (36, 150g) in Et\textsubscript{2}O (200ml) was added carefully to MeMgI (1.5 molar excess) in Et\textsubscript{2}O (250ml), in a 3-necked flask (3000ml) fitted with a stirrer and reflux condenser. When the addition was complete (ca 30 minutes) the reaction mixture was heated under reflux for one hour. The reaction mixture was then poured carefully into NH\textsubscript{4}Cl (aq.) and the product isolated by extraction with Et\textsubscript{2}O.

The residue after removal of the solvent was a mixture of the isomers (GLC, Carbowax 20M) of 4-tert-butyl-1,2-dimethylocyclohexanol (44, 150g, 90%) v\textsubscript{max} 3450, 1195, 1095, 1000 cm\textsuperscript{-1};

NMR \delta 1.6 (1H; C-H); 1.15 (e, 3H; COH-CH\textsubscript{2}); 1.03 and 1.00
(two doublets, J6Hz, 3H; CH-CH\textsubscript{2}); 0.85(s, 9H; tert-butyl); 1.0-1.8 ppm (methylene groups).

4-tert-Butyl-1,2-dimethylocyclohexene (45).

The dimethyl alcohol (44, 150g) was dehydrated with iodine (1.0g) by heating to 150\textdegree and distilling off the water
as it was formed. When water stopped being distilled off
the product was poured into Et₂O and washed with NaHSO₃
(aq.). Removal of the solvent and distillation gave a 4:1
mixture (130g) of the dimethyl-alkene (45) and 5-tert-butyl-
2,3-dimethylcyclohexene NMR δ 5.35 (s, 3H; C=CH₂);
1.64 (s, WH/2 6Hz, 3H; C=C-C₂H₅); 1.00 (d, 37Hz; CH₂-CH₃);
0.88 (s, 9H; tert-butyl); 0.9-2.0 ppm (methylene groups).
Spinnng band fractionation gave GLC pure (carbowax 4000)
4-tert-butyl-1,2-dimethylcyclohexene (45, 60g, 40%)
λ<sub>max</sub> 1480, 1240, 1115 cm⁻¹; NMR δ 1.60 (s, WH/2, 6Hz; C=CH₃);
0.85 (s, 9H; tert-butyl); 1.0-2.0 ppm (methylene groups).

Procedures used to oxidize the alkenes.

(a) Permanganate. To a vigorously stirred mixture
of alkenes (0.1 mole) in tert-butanol (1000ml), H₂O (200ml) and
ice (500g) at -10° was added a solution of KMnO₄ (23.4g) and
NaOH (5g) in water (800ml) at 0°. After 3-5 minutes the
excess KMnO₄ was reduced by the addition of NaHSO₃ and the
mixture filtered through Celite 545 Filteraid to remove the
MnO₂. The filtrate was evaporated down to 500-600ml and
the product extracted into Et₂O. The residue after removal
of the Et₂O was then chromatographed and (or) crystallized.

(b) Performic acid. Alkenes (0.05 mole) was added
to a solution of H₂O₂ (10.5ml, 30%) in formic acid (48ml, 90%)
maintaining the temperature over the addition period (ca. 30 minutes) at 40°-45°, and for one hour thereafter. After standing 12 hours the formic acid was removed by distillation and the residue treated with NaOH (6.5 g) in water (12 ml). The product was isolated by means of Et₂O and purified by chromatography and/or crystallization.

(c) Iodine-silver acetate. Iodine (11.7 g) was added portionwise to a mixture of alkene (0.09 mole) and silver acetate in AcOH (glacial, 300 ml). When all the iodine had been absorbed (ca. one hour) water (1.8 ml) in AcOH (50 ml) was added and the reaction mixture heated to 90° for 3 hours. After cooling, NaCl was added and the silver salts removed by filtration. The residue, after removal of the AcOH, was reacted with KOH (13 g) in MeOH (200 ml) and H₂O (20 ml). After standing overnight the product was isolated by extraction with pentane and purified by chromatography and/or crystallization.

In all cases the diols were purified by crystallization from Et₂O-pentane. Column chromatography was on 5% deactivated alumina, eluting with mixtures of Et₂O and pentane.

Oxidation of 4-tert-Butylcyclohexene (31).

(a) Oxidation of alkene (31, 27 g) with KMnO⁴ gave a mixture of two diols which were separated by fractional
crystallization from Et₂O–pentane.

4α-tert-Butylcyclohexane-1α,2α-diol (48, 11.3 g) m115°–116°

\[
\text{\( \nu_{\text{max}} \) 3360, 1123, 1076, 1068 cm}^{-1}; \text{ NMR: 3.99 (WH/2 8Hz, 1H; CH-OH); 3.57 (WH/2 18Hz, 1H; CH-OH); 2.5 (2H; 0-H); 0.88 (s, 9H; tert-butyl); 0.9–2.0 ppm (methylene groups). Found: C, 69.8; H, 11.9. C₁₀H₂₀O₂ requires C, 69.7; H, 11.7.}
\]

4α-tert-Butyl-cyclohexane-1β,2β-diol (49, 1.5 g) m73°–75°

\[
\text{\( \nu_{\text{max}} \) 3350, 1107, 1079, 1067 cm}^{-1}; \text{ NMR: 3.99 (WH/2 18Hz, 1H; CH-OH); 3.57 (WH/2 18Hz, 1H; CH-OH); 2.4 (2H; 0-H); 0.86 (s, 9H; tert-butyl); 0.9–1.9 ppm (methylene groups). Found: C, 69.9; H, 11.9. C₁₀H₂₀O₂ requires C, 69.7; H, 11.7.}
\]

(b) Oxidation of 31(5 g) with performic acid gave

4α-tert-butyl-cyclohexane-1α,2α-diol (46, 4 g) m138°–140°

(Lit. 45 137–139°); \( \nu_{\text{max}} \) 3300, 1050, 1030, 1020, 998 cm}^{-1}; \text{ NMR: 3.83 (WH/2 12Hz, 2H; CH-OH); 0.87 (s, 9H; tert-butyl); 1.2–1.8 (methylene groups).}

Oxidation of 4-tert-butyl-1-methylocyclohexene (33).

(a) Oxidation of 33(12.5 g) with KMnO₄ gave two diols which were separated by chromatography on alumina (500 g).

Et₂O–pentane(7:3) eluted 4α-tert-butyl-1β-methylocyclohexane-1α,2α-diol (52, 8.9 g) m77°–79°; \( \nu_{\text{max}} \) 3360, 1060, 1028, 997,
\[ 915 \text{ cm}^{-1}; \text{NMR } \delta 3.33(\text{WH/2 } 16\text{Hz}, 1\text{H}; \text{CH}-\text{OH}); 2.2(2\text{H}; 0-\text{H}); 1.25(s, 3\text{H}; \text{COH-CH}_3); 0.87(s, 9\text{H}; \text{tert-butyl}); 1.0-1.9 \text{ ppm (methylene groups). Found: C, 70.9; H, 12.0. } \text{C}_{11}\text{H}_{22}\text{O}_2 \text{ requires C, 70.9; H, 11.0. } \text{Et}_2\text{O eluted } 4\alpha-\text{tert-butyl-1-}\alpha-\text{methylcyclohexane-1,2-}\text{dial (53, 0.2g) m.99-101; } v_{\max } 3400, 1170, 1135, 1055, 1040 \text{ cm}^{-1}; \text{NMR } \delta 3.67(\text{WH/2 } 7\text{Hz}, 1\text{H}; \text{CH}-\text{OH}); 2.3(2\text{H}; 0-\text{H}); 1.22(s, 3\text{H}; \text{COH-CH}_3); 0.87(s, 9\text{H}; \text{tert-butyl}); 1.1-2.0 \text{ (methylene groups). Found: C, 71.1; H, 12.1. } \text{C}_{11}\text{H}_{22}\text{O}_2 \text{ requires C, 70.9; H, 11.9.} \]

(b) Oxidation of 33(12g) with performic acid gave two diols separated by chromatography. \text{Et}_2\text{O-pentane}(4:1) eluted \(4\alpha-\text{tert-butyl-1-}\alpha-\text{methylcyclohexane-1,2-}\text{dial (50, 4.3g) m.117-119}(\text{Lit. } 43_117-118.5'); v_{\max } 3350, 1.75, 1055, 1040, 1015 \text{ cm}^{-1}; \text{NMR } \delta 3.63(\text{WH/2 } 7\text{Hz}, 1\text{H}; \text{CH}-\text{OH}); 1.6(2\text{H}; 0-\text{H}); 1.26(s, 3\text{H}; \text{COH-CH}_3); 0.87(s, 9\text{H}; \text{tert-butyl}); 1.1-1.8 \text{ ppm (methylene groups). } \text{Et}_2\text{O eluted } 4\alpha-\text{tert-butyl-1-}\alpha-\text{methylcyclohexane-1,2-}\text{dial (51, 1.4g) m.114-116}(\text{Lit. } 43_115.5-116'); v_{\max } 3350, 1.75, 1075, 955 \text{ cm}^{-1}; \text{NMR } \delta 3.53(\text{WH/2 } 19\text{Hz}, 1\text{H}; \text{CH}-\text{OH}); 2.3(2\text{H}; 0-\text{H}); 1.17(3\text{H}; \text{COH-CH}_3); 0.87(s, 9\text{H}; \text{tert-butyl}); 1.0-2.0 \text{ ppm (methylene groups).} \]

(c) Oxidation of 33(13.4g) with iodine-silver acetate gave a mixture of two diols. \(4\alpha-\text{tert-Butyl-1-}\alpha-\text{methylcyclohexane-1,2-}\text{dial (52, 7.6g) and } 4\alpha-\text{tert-butyl-}
-1α-methylcyclohexane-1β,2β-diol (53, 1.6g).

Oxidation of 4-tert-butyl-2-methylcyclohexene (42).

(a) Oxidation of 42 (7.6g) with KMnO₄ gave two diols (56 and 57) by NMR. The diols could not be separated by chromatography or crystallization. The mixture was acetylated and the mono-acetates separated by column chromatography. Hydrolysis then gave the two diols.

Acetylation of the diols 56 and 57.

A solution of the diol mixture (7.0g), acetic anhydride (4ml) and pyridine (4ml) in benzene was stirred for 15 hours. The products were then isolated by extraction with Et₂O. After removal of the solvent the residue was columned on alumina (10% deactivated, 200g). Et₂O-pentane (1:99) eluted 4α-tert-butyl-2α-methylcyclohexane-1α-acetoxy-2β-ol (58, 5.5g) m. 85°-87°; vmax 3450, 1700, 1240, 1025, 985 cm⁻¹; NMR s 4.63 (4H/2 15Hz, 1H; CH₃CO); 2.10 (4, 3H; CO-CH₃); 1.8 (1H; 0-H); 1.18 (4, 3H; COH-CH₃); 0.85 (4, 9H; tert-butyl); 1.1-2.1 ppm (methylene groups). Et₂O-pentane (1:18) eluted 4α-tert-butyl-2β-methylcyclohexan-1α-acetoxy-2α-ol (59, 1.2g) vmax 3500, 1740, 1720, 1240, 1115, 1040, 1020 cm⁻¹; NMR δ 4.77 (4H/2 6Hz, 1H; CH₃CO); 2.10 (4, 3H; CO-CH₃); 2.0
(1H; 0-H); 1.25 (s, 3H; COH-CH₃) 0.87 (s, 9H; tert-butyl); 1.2-2.0 ppm (methylene groups).

**Hydrolysis of the acetates** (58 and 59).

The acetate (lg) was stirred overnight with KOH (lg) in MeOH (20mL) and water (4mL). The product was isolated by extraction with Et₂O and purified by crystallization from Et₂O-pentane.

4-tert-Butyl-2-α-methylcyclohexane-1',2'-diol (57, 0.6g)
m. 80°-82°; νmax 3350, 1130, 1085, 1070, 1020 cm⁻¹;
NMR: 3.28 (m, 2H, 1H; CH-OH); 2.1 (2H; 0-H); 1.25 (s, 3H; COH-CH₃); 0.83 (s, 9H; tert-butyl); 1.0-2.0 ppm (methylene groups).
Found: C, 70.6; H, 12.0. C₁₁H₂₂O₂ requires: C, 70.9; H, 11.9.

4-tert-Butyl-2β-methylcyclohexane-1,2-α-diol (56, 0.6g)
m. 88°-90°; νmax 3350, 1095, 1060, 1040, 1015 cm⁻¹;
NMR: 3.56 (m, 2H, 1H; CH-OH); 2.6 (2H; 0-H); 1.22 (s, 3H; COH-CH₃); 0.85 (s, 9H; tert-butyl); 1.0-2.0 ppm (methylene groups).
Found: C, 70.7; H, 12.2. C₁₁H₂₂O₂ requires: C, 70.9; H, 11.9.

(b) Oxidation 42 (12.2g) with performic acid gave a mixture of two diols separated by chromatography.
Et₂O-pentane (3:2) eluted 4-tert-butyl-2α-methylcyclohexane-
1α,2β-diol (54, 6.0g) m. 113°-114°; νmax 3450, 1145, 1040, 1005,
970 cm⁻¹; NMR s 3.50 (vH/2 6 Hz; 1H; CH₂OH); 1.7 (2H; 0-1); 1.25 (s, 3H; CON-CH₃); 0.85 (s, 9H; tert-butyl); 1.2-1.9 ppm (methylene groups). Found: C, 70.5; H, 12.2. C₁₁H₂₂O₂ requires: C, 70.7; H, 12.0. Et₂O eluted 4α-tert-butyl-2β-methylcyclohexene-1α,2α-diol (55,1.0g) m.135⁰-137⁰; vmax 3350, 1105, 1075, 940 cm⁻¹; NMR s 3.47 (vH/2 17 Hz, 1H; CH- OH); 2.3 (2H; 0-1); 1.18 (s, 3H; CON-CH₃); 0.85 (s, 9H; tert-butyl); 0.9-1.9 ppm (methylene groups). Found: C, 70.8; H, 11.9. C₁₁H₂₂O₂ requires: C, 70.9; H, 11.9.

Oxidation of 4-tert-butyl-1,2-dimethylcyclohexene (45).

(a) Oxidation of 45 (8.3g) gave two diols which were separated by chromatography. Et₂O-pentane (1:2) eluted 4α-tert-butyl-1α,2β-dimethylcyclohexene-1α,2α-diol (62,3.0g) m. 88⁰-91⁰; vmax 3400, 1190, 1150, 1130, 1100, 1050, 930, 912 cm⁻¹; NMR s 2.2 (2H; 0-1); 1.20 (s, 6H; CON-CH₃); 0.85 (s, 9H; tert-butyl); 0.9-2.0 ppm (methylene groups). Found: C, 72.0; H, 12.0. C₁₂H₂₄O₂ requires: C, 71.9; H, 12.1.

Et₂O-pentane (1:2) eluted 4α-tert-butyl-1α,2α-dimethyl -cyclohexane-1α,2β-diol (63,2.7g) m. 106⁰-108⁰; vmax 3440, 1170, 1130, 1110, 1000, 950 cm⁻¹; NMR s 2.3 (2H; 0-1); 1.20 (s, 3H; CON-CH₃); 1.18 (s, 3H; CON-CH₃); 0.85 (s, 9H; tert-butyl); 1.1-1.9 ppm (methylene groups). Found: C, 71.7; H, 11.9. C₁₁H₂₄O₂ requires: C, 71.9; H, 12.1.
(b) Performic acid oxidation of 45(13g) yielded one diol which was purified by crystallization from Et₂O-pentane.

4α-tert-Butyl-1β,2α-dimethylcyclohexane-1α,2β-di01
(60,9,0g)m.121°-123°; ν max 3450, 1180, 1145, 1120, 1055, 960, 950, 912, 827 cm⁻¹; NMR δ 1.23 (q 6H; COH-CH₃); 0.87(s, 9H; tert-butyl); 1.2-1.7 ppm(methylene groups). Found: C, 71.8; H, 12.0. C₁₂H₂₄O₂ requires: C, 71.9; H, 12.1.

4α-tert-Butylocyclohexanol-2α-benzoxloxy-1α-ol(64).

To a solution of diol(48,4.0g) and pyridine(10m) in benzene(5ml) was added benzoylchloride(4.0g) in benzene(5ml). The reaction mixture was stirred for 2 hours then the product isolated by means of Et₂O. The crude product was purified by crystallization from pentane.

4α-tert-Butylocyclohexanol-2α-benzoxloxy-1α-ol(64,5.0g,70%) m.86°-90°; ν max 3625, 1725, 1270, 1100, 1030 cm⁻¹;
NMR δ 8.08(Wh/2 11Hz, 2H; Ar-H); 7.47(Wh/2 9Hz, 3H; Ar-H);
5.03(Wh/2 16Hz, 1H; CH-OBz); 4.17(Wh/2 9Hz, 1H; CH-OBz);
2.0(1H; 0-H); 0.92(q, 9H; tert-butyl); 1.2-2.0(methylene groups).
Found: C, 73.6; H, 8.8. C₁₇H₂₄O₃ requires: C, 73.9; H, 8.7.

4α-tert-Butyl-2α-benzoxloxy-cyclohexanone(65).

The mono-benzoate(64,2.5g) was oxidized with Jones
Reagent in acetone by the procedure previously described.

4\textsuperscript{-}tert-Butyl-2\textsuperscript{-}benzozoxy-cyclohexanone(65, 2.0g, 80\% )
m. 127-128\(^{0}\); \(\nu\max 1745, 1725, 1275, 1125, 710 \text{ cm}^{-1}\);
NMR \( \delta 8.08(\text{Wh/2 1H}, 2\text{H; Ar-\text{H}}); 7.47(\text{Wh/2 9H}, 3\text{H; Ar-\text{H}}); 5.47(\text{Wh/2 17H}, 1\text{H; CH-OBz}); 9.67(s, 9\text{H; tert-butyI}); 1.5-2.6 \text{ ppm(methylene groups)}. \) Found: C, 74.6; H, 8.3.
C\textsubscript{17}H\textsubscript{22}O\textsubscript{3} requires: C, 74.4; H, 8.1.

4-tert-Butyl-2-acetoxy-cyclohexanone(66).

A mixture of ketones(29, 10.0g) and Pb(OAc)\textsubscript{4} in benzene was heated under reflux for 8 hours. After this time the lead salts were filtered off and the product isolated by means of Et\textsubscript{2}O. The oily residue(10.5g) was chromatographed on alumina(5\%, 400g). Pentane eluted starting ketone(29, 3.0g). Benzene-pentane(1:1) eluted fractions consisting of mixtures (by TLC) of two compounds. The IR spectra were consistent with the compounds being the two isomers of 4-tert-butyI-2-acetoxy-cyclohexanone(66) \(\nu\max 1730, 1720, 1250, 1075 \text{ cm}^{-1}\).

4\textsuperscript{-}tert-Butyl-cyclohexan-1\textsuperscript{\beta},2\textsuperscript{-}diol(47).\textsuperscript{45}

(a) To a solution of the acetoxy ketones(66) in propan-2-ol(100ml) was added sodium(5g) and the reaction mixture heated under reflux for one hour. The product was
isolated by extraction with $\text{Et}_2\text{O}$. The oily residue after removal of the solvent was chromatographed on alumina (5%, 250g). $\text{Et}_2\text{O}$ eluted a mixture (0.3g, 1:1) of 4-tert-butylcyclohexane-1$\alpha$,2$\alpha$-diol (48) and 1$\beta$,2$\beta$-diol (49). Further elution with $\text{Et}_2\text{O}$ yielded 4-tert-butylcyclohexane-1$\beta$,2$\alpha$-diol (47, 0.7g), 104-106$^\circ$ (Lit. 12105$^\circ$-107$^\circ$); $\nu$ max 3250, 1110, 1075, 1060, 985 cm$^{-1}$; NMR $\delta$ 3.50 (4H/2 16Hz, 2H; OH-OH); 2.6 (2H; 0-OH); 0.87 (s, 9H; tert-butyl); 0.9-2.2 ppm (methylene groups).

(b) Sodium (5g) was added to a solution of 4-tert-butyl-cyclohexane-2$\alpha$-benzol oxy-1-one (2g) in isopropanol (100ml). When the addition was complete the reaction mixture was refluxed for one hour. The product was isolated by means of $\text{Et}_2\text{O}$ and chromatographed on alumina (5%, 100g). $\text{Et}_2\text{O}$ eluted a mixture (1:1) of diols (48) and (49) (0.4g) followed by diol (47) (0.8g).

4-tert-Butyl-1$\beta$-methylcyclohexan-2-one-1$\alpha$-ol (68).

A mixture of 1-methyl diol (50, 5.0g) and $\text{KMnO}_4$ (8.0g) was heated under reflux in acetone for 8 hours. The product was isolated by means of $\text{Et}_2\text{O}$ and chromatographed on alumina (5%, 250g). $\text{Et}_2\text{O}$-pentane (3:7) eluted 4-tert-butyl-1$\beta$-methylcyclohexan-2-one-1$\alpha$-ol (68, 2.2g, 45%)
\[ \text{max} \ 3420, \ 1710, \ 1185, \ 1140, \ 980 \ \text{cm}^{-1}; \quad \text{NMR} \ \delta \ 2.2(1H; \text{O-H}); \ 1.23(3H; \text{CH}_3; \text{COH-CCH}_3); \ 0.85(3H; \text{tert-butyl}); \ 1.2-2.7 \ \text{ppm} \quad (\text{methylene groups}). \]

4-tert-Butyl-1α-methylcyclohexan-2-one-1β-ol (67).

The 1-methyl diol (52, 3.0g) was oxidized with Jones reagent in acetone at \(-10^\circ\) to \(-15^\circ\). The product was isolated by extraction with Et\(_2\)O and chromatographed on alumina (5%, 150g). Et\(_2\)O-pentane (3:7) eluted 4-tert-butyl-1α-methylcyclohexan-2-one-1β-ol (67, 1.7g, 60%) \[ \text{max} \ 3500, \ 1715, \ 1360, \ 1140, \ 990 \ \text{cm}^{-1}; \quad \text{NMR} \ \delta \ 4.2(1H; \text{O-H}); \ 1.37(3H; \text{CH}_3; \text{COH-CCH}_3); \ 0.90(3H; \text{tert-butyl}); \ 1.1-2.6 \quad (\text{methylene groups}). \]

Reactions of a Methyl Grignard on the 1α-methyl ketol (68).

To a stirred solution of MeMgI (3 molar excess) in Et\(_2\)O (15ml) was carefully added ketol (68, 1.5g) in Et\(_2\)O (10ml). When the addition was complete the reaction mixture was heated under reflux for one hour. The product was isolated by extraction with Et\(_2\)O and chromatographed on alumina (5%, 100g). Et\(_2\)O-pentane (3:7) eluted the dimethyl-1α,2β-diol (60, 1.1g, 60%). Et\(_2\)O-pentane (1:1) eluted the dimethyl-1α,2α-diol (62, 0.3, 15%).
Reaction of a Methyl Grignard on the 1α-methyl ketol (67).

To a stirred solution of MeMgI (3 molar excess) in Et₂O (15ml) was added ketol (67, 1.5g) in Et₂O (10ml). When the addition was complete the reaction mixture was heated under reflux for one hour. The product was isolated by extraction with Et₂O and chromatographed on alumina (5%, 100g).

Et₂O-pentane (1:1) eluted the dimethyl-1β,2β-diol (63, 1.20g 75%).

Et₂O eluted an unknown dimethyl diol which was assigned the 1β,2α-stereochemistry.

4-tert-Butyl-1α,2β-dimethylcyclohexane-1β,2α-diol (61, 0.14g, 8%)

mp. 117°-119°; ν max 3450, 1127, 1114, 1100, 987 cm⁻¹;

NMR δ 1.3(2H; O-H); 1.30(δ, 3H; COH-CH₃); 1.28(δ, 3H; COH-CH₃);

0.85(δ, 9H; tert-butyl); 0.9-1.8 (methylene groups).

Found: C, 71.8; H, 12.0. C₁₂H₂₄O₂ requires: C, 71.9; H, 12.1.

Procedure for hydroboration.

To a stirred mixture of NaN₃₄ (1g) in diglyme (20ml) was added BF₃-etherate (5ml) in diglyme (5ml). The diborane generated was carried into a solution of alkene (6g) in dry THF (50ml), by a stream of nitrogen. The gas stream was then passed into acetone before being vented into the atmosphere. When the addition was complete the diborane
generator was heated to 70° for one hour to ensure all the
diborane was carried into the reaction vessel. After cooling,
water was added to the reaction mixture to destroy unreacted
diborane. The solution is then stirred for one hour with
a solution of KOH(3N, 5 ml) and H₂O₂(30%, 5 ml). The product
was then isolated by extraction with Et₂O.

(a) Hydroboration of the 4-tert-butyl-2-methylcyclohexene

The crude product (5.4 g) was shown by NMR to consist
of a mixture (3:1) of the alcohols 69 and 70. The alcohols
were separated by chromatography on alumina (5%, 300 g).
Et₂O-pentane (1:40) eluted GLC pure (carbowax 20M)
4α-tert-butyl-2β-methylcyclohexan -1α-ol[43] (70, 1.0 g)
m. 63-64; max 3400, 1060, 1010, 990, 940 cm⁻¹;
NMR 3.68 (Wh/2 7 Hz, 1H; CH-OH); 1.5 (1H; O-H); 0.96
( d, J7 Hz, 3H; CH-CH₃); 0.83 (s, 9H; tert-butyl); 1.0-1.9 ppm
(methylene groups). Similarly Et₂O-pentane (1:40) eluted
GLC pure 4α-tert-butyl-2α-methylcyclohexan -1β-ol[43] (69, 1.1 g)
max 3400, 1235, 1085, 1060, 1045 cm⁻¹; NMR 3.06 (Wh/2
17 Hz, 1H; CH-OH); 1.7 (1H; O-H); 1.05 (s, Wh/2 2.5 Hz; CH-CH₃);
0.83 (s, 9H; tert-butyl); 0.9-2.0 ppm (methylene groups).
(b) Hydroboration of 4-tert-butyl-1-methylcyclohexene(33).

The product was shown by NMR to consist of a mixture (3:1) of alcohols 72 and 71. The alcohols could not be separated by chromatography on alumina. The NMR data was obtained from the spectra of the mixture. 4-tert-Butyl-1α-methylcyclohexan - 2β-ol(71) 43 NMR 3.80 (W/2 6Hz, 1H; CH-CH₃); 0.93 (d, J7Hz, 3H; CH-CH₃); 0.85 (3, 9H; tert-butyl).

4α-tert-Butyl-1β-methylcyclohexan -2-ol(72) 43 NMR δ 3.07 (W/2 16Hz, 1H; CH-CH₃); 1.03 (3, W/2 2.5, 3H; CH-CH₃); 0.85 (3, 9H; tert-butyl).

Oxidation with CrO₃-pyridine.

The CrO₃-pyridine complex was prepared by adding CrO₃ (5g) to pyridine (40ml) at 10°. The alcohol (1.0g) in pyridine (10ml) was then added to the 8 molar excess of complex in pyridine, and the mixture stirred for 12 hours. The product was isolated by extraction with Et₂O.

(a) 4α-tert-Butyl-2α-methylcyclohexanone(73). 38

Preparative GLC (FFAP) of the material from the CrO₃-pyridine oxidation of the alcohol (69) yielded GLC pure (PEGA) 4-tert-butyl-2-methylcyclohexanone (73) λ max 1715, 1155, 1100.
1005 cm\(^{-1}\); NMR \(\delta \) 1.03 (d, J 6 Hz, 3H; CH-CH\(_3\)); 0.90 (s, 9H; tert-butyl); 1.0-2.6 ppm (methylene protons).

(b) \(4\alpha\)-tert-Butyl-2\(\beta\)-methylcyclohexanone (74).\(^{38}\)

Preparative GLC (FFAP) of the material from the CrO\(_3\)-pyridine oxidation of alcohol (70) yielded GLC pure (PEG) \(4\alpha\)-tert-butyl-2\(\beta\)-methyl-cyclohexanone (74) \(\nu\) max 1715, 1210, 1155, 1100, 965 cm\(^{-1}\); NMR \(\delta \) 1.15 (d, J 7 Hz, 3H; CH-CH\(_3\)); 0.90 (s, 9H; tert-butyl); 1.2-2.7 ppm (methylene groups).

(c) \(5\alpha\)-tert-Butyl-2\(\alpha\)-methyl-cyclohexanones (75 and 76).\(^{43}\)

The alcohol mixture (3:1) of 72 and 71 was oxidised with CrO\(_3\)-pyridine to produce a mixture (3:1) of ketones assigned the same stereochemistry as the alcohols. The ketones 75 and 76 were separated by chromatography on silica (200g). Et\(_2\)O-pentane (1:50) eluted GLC pure (PEG) \(5\alpha\)-tert-butyl-2\(\alpha\)-methylcyclohexanone (76) \(\nu\) max 1715, 1215, 1180, 1155 cm\(^{-1}\); NMR \(\delta \) 1.02 (d, J 6 Hz, 3H; CH-CH\(_3\)); 0.88 (s, 9H; tert-butyl); 1.1-2.7 ppm (methylene groups). Et\(_2\)O-pentane (1:40) eluted GLC pure (PEG) \(5\alpha\)-tert-butyl-2\(\alpha\)-methylcyclohexanone (75) \(\nu\) max 1715, 1220, 1165 cm\(^{-1}\); NMR \(\delta \) 1.15 (d, J 7 Hz, 3H; CH-CH\(_3\)); 0.90 (s, 9H; tert-butyl) 1.2-2.7 ppm (methylene groups).
Methylation procedure for the preparation of the dimethyl-cyclohexanones (77 and 78).

Sodium (0.5g) was added to liquid ammonia (20ml) containing a trace of ferric chloride. The reaction mixture was stirred until all the blue colour had disappeared. The ammonia was replaced by Et₂O (20ml). The ketone (3.0g) was added in Et₂O (10ml) and the reaction mixture heated under reflux for 3 hours. NaI (2.5g) was added and the reaction mixture heated under reflux a further 3 hours. The product was isolated by extraction with Et₂O and consisted of a mixture of starting material and dimethyl ketone. The dimethyl ketone was purified by preparative glc (PFAP).

5α-tert-Butyl-2,2-dimethylcyclohexanone (78) \(^{J}\) max 1715, 1130, 1090 cm\(^{-1}\); NMR δ 1.13 (s, 3H; -CH\(_3\)); 1.05 (s, 3H; -CH\(_3\)); 0.89 (s, 9H; tert-butyl); 1.1-2.6 ppm (methylenic groups).
Found: C, 79.16; H, 12.10. \(\text{C}_{12}\text{H}_{22}\text{O}\) requires: C, 79.06; H, 12.17.

4α-tert-Butyl-1,1-dimethylcyclohexanone (77) \(^{J}\) max 1715, 1155, 1100, 985 cm\(^{-1}\); NMR δ 1.15 (s, 3H; -CH\(_3\)); 1.05 (s, 3H; -CH\(_3\)); 0.90 (s, 9H; tert-butyl); 1.2-2.6 ppm (methylenic groups).
Found: C, 78.94; H, 12.25. \(\text{C}_{12}\text{H}_{22}\text{O}\) requires: C, 79.06; H, 12.17.
Preparation of the cyclic sulphites of the cyclohexane-diols.

Freshly distilled SOCl₂(0.3g) was added to a solution of diol(0.2g) in dry CH₂Cl₂(20ml). For the preparation of the unsubstituted diol cyclic sulphites the reaction mixture was stirred for 10 minutes before being worked up. For the remainder of the cyclic sulphites the reaction mixture was heated under reflux for 1 hour before being worked up. The reaction mixture was worked up by pouring into pentane and washing with water and NaHCO₃(aq.). The cyclic sulphites were purified and the isomers separated by chromatography on silica(20g). Elemental analysis were obtained for mixtures of the A and B-isomers. The isomers were identified by TLC and NMR. The position of the tert-butyl group in the NMR varied from 0.83-0.88 ppm. The NMR data obtained from spectra of the pure isomers where they were separated, this is indicated by an asterisk.

4α-tert-Butylcyclohexane-1α,2α-diol(48) cyclic sulphites

(A:B, 1:1)M(A) 55⁰-56⁰; max 1200, 965, 840, 780 cm⁻¹;
NMR δ(B) 4.92(wh/2 1kHz, 2H; CH₂-OSO₂); (A) 4.53 ppm(wh/2 9Hz; 2H; CH₂-OSO₂). Found: C, 64.5; H, 10.0; S, 17.0. \(\text{C}_{10}\text{H}_{18}\text{S} \text{O}_3\) requires: C, 64.5; H, 9.7; S, 17.2.
4α-tert-Butylcyclohexane-1α,2α-diol (47) cyclic sulphites
(A:B;1:2)m. (B) 68°-71°; J max 1200, 980, 950, 940, 770,
710 cm⁻¹; NMR* (A) δ 5.00 (Wh/2 10Hz, 2H; CH-OSO); (B) 4.53
(Wh/2 13Hz, 2H; CH-OSO). Found: C, 64.8; H, 10.1; S 16.9.
C₁₀H₁₈SO₃ requires: C, 64.5; H, 9.7; S, 17.2.

4α-tert-Butylcyclohexane-1β,2α-diol (49) cyclic sulphydes
(A:B;1:2)m. (B) 68°-71°; J max 1210, 1010, 1000, 880 cm⁻¹; NMR δ 4.17 (Wh/2 16Hz, 1H; CH-OSO); 3.67 ppm (Wh/2 17Hz, 1H; CH-OSO). Found: C, 65.2;
H, 9.9; S, 16.6. C₁₀H₁₈SO₃ requires: C, 64.5; H, 9.7; S, 17.2.

4α-tert-Butyl-1α-methylcyclohexane-1α,2α-diol (52)
cyclic sulphites (A:B;1:2); J max 1200, 980, 945, 885 cm⁻¹;
NMR* (A) δ 4.30 (q, J₂ 6.5Hz, J₁ 10Hz, 1H; CH-OSO); 1.38 (s, 3H;
-CH₃); (B) 4.63 (q, J₂ 6.5Hz, J₁ 10Hz, 1H; CH-OSO);
1.68 ppm (s, 3H; -CH₃). Found: C, 66.2; H, 10.4; S, 15.8.
C₁₁H₂₀SO₃ requires: C, 65.9; H, 10.1; S, 16.0.

4α-tert-Butyl-1α-methylcyclohexane-1α,2α-diol (53)
cyclic sulphites (A:B;1:1); J max 1210, 1030, 975, 910, 880 cm⁻¹;
NMR* (A) δ 4.77 (Wh/2 7Hz, 1H; CH-OSO); 1.55 (s, 3H; -CH₃);
(B) 4.30 (Wh/2 7Hz, 1H; CH-OSO); 1.53 ppm (s, 3H; -CH₃).
Found: C, 66.2; H, 10.4; S, 15.5. C₁₁H₂₀SO₃ requires:
C, 65.9; H, 10.1; S, 16.0.
4α-tert-Butyl-1α-methylicyclohexane-1β,2α-diol (51)
cyclic sulphites (A:B, 1:1); ν max 1210, 1100, 930, 920, 775 cm⁻¹;
NMR (A) δ 3.83 (s, 3H; CH₃), 1.53 (s, 3H; CH₃) 4.37 (s, 3H; CH₃) ppm;

4α-tert-Butyl-2β-methylicyclohexane-1α,2α-diol (56)
cyclic sulphites (A:B, 1:1); ν max 1210, 910, 890, 770 cm⁻¹;
NMR (A) δ 4.20 (s, 3H; CH₃), 1.45 (s, 3H; CH₃);
(B) 4.65 (s, 3H; CH₃), 1.58 ppm (s, 3H; CH₃).
Found: C, 66.1; H, 10.2; S, 15.6. C₁₁H₂₀SO₃ requires:
C, 65.9; H, 10.1; S, 16.0.

4α-tert-Butyl-2β-methylicyclohexane-1β, 2β-diol (57)
cyclic sulphites (A:B, 1:1); ν max 1200, 950, 940, 815 cm⁻¹;
NMR (A) δ 4.73 (d, J 6Hz, 3H; CH₃), 1.70 (s, 3H; CH₃);
(B) 4.27 (d, J 8Hz, 3H; CH₃), 1.40 ppm (s, 3H; CH₃).
Found: C, 66.2; H, 10.4; S, 15.7. C₁₁H₂₀SO₃ requires:
C, 65.9; H, 10.1; S, 16.0.

4α-tert-Butyl-2β-methylicyclohexane-1β, 2α-diol (55)
cyclic sulphites (A:B, 1:1); ν max 1210, 945, 930, 780 cm⁻¹;
NMR (A) δ 4.38 (m, 3H; CH₃), 1.25 (s, 3H; CH₃);
(B) 3.78 (d, J 17Hz, 3H; CH₃), 1.52 (s, 3H; CH₃).

4α-tert-Butyl-1β,2β-dimethylicyclohexane-1α,2α-diol (62)
cyclic sulphites (A:B, 1:1); ν max 1210, 890, 710 cm⁻¹;
NMR (A) 1.40 and 1.28 (s, 3H; -CH\textsubscript{3}); (B) 1.57 and 1.48 ppm (s, 3H; -CH\textsubscript{3}). Found: C, 67.6; H, 10.6; S, 14.5.

C\textsubscript{12}H\textsubscript{22}SO\textsubscript{3} requires: C, 67.2; H, 10.4; S, 15.0.

4-\textsuperscript{3}t-Butyl-1,\textsuperscript{2}\alpha,2\alpha\textsuperscript{-dimethylcyclohexane-1\beta,2\beta\textsuperscript{-diol (63)}}

Cyclic sulphites (A:B, 1:1); \nu \text{max} 1200, 910, 895, 810, 790 cm\textsuperscript{-1}; NMR (A) 1.58 and 1.48 (s, 3H; -CH\textsubscript{3}); (B) 1.30 and 1.20 (s, 3H; -CH\textsubscript{3}). Found: C, 67.3; H, 10.4; S, 14.7. C\textsubscript{12}H\textsubscript{22}SO\textsubscript{3} requires: C, 67.2; H, 10.3; S, 15.0.

4,4\textsuperscript{1}-Dimethyl- and 4,4\textsuperscript{1}-dimethoxy-benzoin (84 and 85).

Freshly distilled aldehyde (0.42 moles) was added to a solution of KCN (0.17 moles) in EtOH (75 ml) and H\textsubscript{2}O (45 ml) and the solution heated under reflux for 5 hours. A small portion was then extracted with Et\textsubscript{2}O and the solid obtained used to seed the remainder of the reaction mixture which was left to crystallize at 4\textdegree for 3-5 hours. The product was collected by filtration and recrystallized from EtOH.

The yield, from this first crystallization, was 35\%-40\% but could be increased by removing EtOH and initiating a second crystallization.

4,4\textsuperscript{1}-Dimethylbenzoin (84) m. 86\textdegree-87\textdegree (Lit. 46\textdegree-89\textdegree)

\nu \text{max} 3400, 1685, 1580, 1070, 860 cm\textsuperscript{-1}; NMR \delta 7.94 (2H; Ar-\textsuperscript{H});
7.37 (8H; Ar-H); 5.97 (1H; CH=OH), 4.6 ppm (1H; O-H).

4,4'-Dimethoxybenzoin (85) m. 112°-114° (Lit. 109°-110°); 
|j_max = 3490, 1680, 1600, 1250, 1175, 1030, 985 cm⁻¹; |
|NMR = 7.85-6.85 (8H; Ar-H); 5.87 (1H; CH=OH); 4.6 (1H; O-H); |
|3.72 and 3.78 ppm (3H; -OCH₃). |

**Benzoin (83).**

Crude benzoin was obtained from the Undergraduate Laboratories and recrystallised from MeOH.

Benzoin (83) m. 134°-135° (Lit. 130°-135°); |j_max = 3400, |
|1685, 1580, 1070, 860 cm⁻¹; |
|NMR = 7.94 (2H; Ar-H); 7.37 (8H; Ar-H); 5.97 (1H; CH=OH); 4.6 ppm (1H; O-H). |

**3,3'-Dichlorobenzoin (86).**

A saturated aqueous solution of KCN (0.25 g) was added to a solution of freshly distilled m-chlorobenzaldehyde (20 g) and the reaction mixture heated under reflux for 30 minutes. MeOH was removed by distillation and the product isolated by means of Et₂O.

3,3'-Dichlorobenzoin (86) m. 62°-65°; |j_max = 3450, 1680, |
|1070, 1000, 790 cm⁻¹; |
|NMR = 7.1 and 7.9 (8H; Ar-H); 5.90 (1H; CH=OH); 4.5 ppm (1H; O-H). |
NaBH₄ reduction of the benzoin (83-86).

NaBH₄ (0.08 moles) was added portionwise to a stirred solution of the benzoin (0.15 moles) in EtOH (160 ml) and the reaction mixture stirred for 30 minutes. The reaction mixture was then diluted with water (150 ml) and heated to boiling. The product crystallized from the reaction mixture after cooling and a final dilution with water (250 ml). The diols were purified by crystallization from Et₂O-pentane. The hydrobenzoins formed by this reduction have the meso-configuration.

meso-Hydrobenzoin (89) m.136⁰-137⁰ (Lit. 49 m.135⁰-136⁰); νmax 3360, 1285, 1040, 1030, 760 cm⁻¹; NMR δ 7.15 (S, 10H; Ar-H); 4.72 (S, 2H; CH₂-OH); 2.0 ppm (2H; O-H).

meso-4,4'-Dimethylhydrobenzoin (90) m.143⁰-144⁰ (Lit. 47 m.145⁰-146⁰); νmax 3500, 1050, 1025, 1014, 814, 720 cm⁻¹; NMR δ 7.13 (S, 8H; Ar-H); 4.71 (S, 2H; CH₂-OH); 2.33 (S, 6H; Ar-CH₃); 2.0 ppm (2H; O-H).

meso-4,4'-Dimethoxyhydrobenzoin (91) m.169⁰-171⁰; νmax 3300, 1614, 1245, 1170, 1020, 830 cm⁻¹; NMR δ 7.22 and 6.92 (d, J 8 Hz; Ar-H); 4.73 (S, 2H; CH₂-OH); 3.80 (S, 6H; Ar-CH₃); 1.6 ppm (2H; O-H).
meso-3,3'-Dichlorohycrobensoin (92) m. 94°-96°;

$\nu_{max}$ 3400, 1575, 1204, 1032, 795, 710 cm$^{-1}$; NMR $\delta$ 7.3-6.9

(8H; Ar-H); 4.75 (s, 2H; CH-OH); 2.5 ppm (2H; 0-H).

Found: C, 59.3; H, 4.7; Cl, 25.1. $C_{14}H_{12}O_2$ Cl requires:

C, 58.9; H, 5.0; Cl, 24.8.

**meso-Hydrobenzoin diacetate (87).**

To meso-hydrobenzoin (29.5g) in benzene (90ml) and pyridine (110ml) was added acetic anhydride (34ml) and the reaction mixture stirred for 15 hours. The product isolated by extraction with Et$_2$O and purified by crystallization from EtOH.

**meso-Hydrobenzoin diacetate (87, 29g, 70%) m. 133°-134°

(Lit. m. 135-136°); $\nu_{max}$ 1740, 1245, 1220, 1045, 765 cm$^{-1}$;

NMR $\delta$ 7.23 (s 10H; Ar-H); 6.10 (s 2H; CH-OAc); 1.97 ppm

( s 6H; CO-CH$_3$).

**meso-4,4'-Dinitrohydrobenzoin diacetate (88).**

meso-Hydrobenzoin diacetate (10g) was added portionwise with stirring to fuming HNO$_3$ (60ml) at -10°. The reaction mixture was stirred for 30 minutes then poured into crushed ice (150g) and left to stand for 2 hours. The product was collected by filtration.
meso-4,4'-Dinitrohydrobenzoin diacetate (88) m. 225°-230°
(Lit. 48 m. 232°); ν max 1740, 1350, 1120, 1040, 700 cm⁻¹;
NMR ≤ 8.22 (d, J 8Hz, 4H; Ar-H); 7.50 (d, J 8Hz, 4H; Ar-H);
5.83 (s, 2H; CH-0Ac); 2.10 ppm (s, 6H; CO-CH₃).

**meso-4,4'-Dinitrohydrobenzoin (93).**

A solution of 4,4'-dinitrohydrobenzoin diacetate (13g)
and H₂SO₄ (240ml, 25%) in EtOH (240ml) was heated under reflux
for 5 hours. The product was allowed to crystallize from
the reaction mixture after removal of the EtOH and dilution
with water.

**meso-4,4'-Dinitrohydrobenzoin (93, 76, 60%) m. 210°-220°
(with decomposition) (Lit. 48 m. 231° Charring); ν max 3500,
1520, 1060, 855, 800, 752 cm⁻¹; NMR ≤ 8.17 (d, J 8Hz, 4H; Ar-H);
7.58 (d, J 8Hz, 4H; Ar-H); 4.83 (s, 2H; CH-0H); 2.4 ppm (2H; O-H).

**Preparation of the hydrobenzoin cyclic sulphites (94-97).**

Distilled SOCl₂ (0.025 moles) was added to a solution of
the diol (0.02 moles) and pyridine (2ml) in CH₂Cl₂ (60ml).
The reaction mixture was then heated under reflux for
10-15 minutes. The one exception was the reaction of the
dimethyl diol (91) which was carried out at 0°. The
products were isolated by extraction with pentane.
Crystallization from Et2O-pentane or EtOH yielded the pure syn-isomers (the S-O and H having a syn-relation). Samples of the anti-isomers were obtained by chromatography on silica. The yield of recovered sulphite was 70-80%, with the crude material consisting of a ca 20:1 mixture of the syn- and anti-isomers.

**meso-Hydrobenzoic cyclic sulphite (94)**

m. 124°-126° (Lit. m. 124°-125.5°); λ max 1220, 965, 940, 785 cm⁻¹; NMR: 7.2 and 6.8 (10H; Ar-\(\overline{H}\)); syn. 6.12 (s, 2H; CH-OSO); anti 5.97 (s, 2H; CH-OSO).

**meso-4,4'-Dinitrohydrobenzoic cyclic sulphite (97)**

m. 180°-184°; λ max 1210, 970, 855, 730, 720 cm⁻¹; NMR 8.09 (d, J3Hz, 4H; Ar-\(\overline{H}\)); 7.17 (d, J3Hz, 4H; Ar-\(\overline{H}\)); syn 6.38 (s, 2H; CH-OSO); anti 6.05 (s, 2H; CH-OSO).

Found: C, 48.4; H, 3.1; S, 8.6; N, 8.0. C\(_{14}\)H\(_{10}\)N\(_{2}\)SO\(_{7}\) requires: C, 48.0; H, 2.9; S, 9.2; N, 8.0.

**meso-4,4'-Dimethylhydrobenzoic cyclic sulphite (95)**

m. 78°-80°; λ max 1210, 960, 934, 765, 720 cm⁻¹; NMR 6.7-7.2 (8H; Ar-\(\overline{H}\)); syn 6.10 (s, 2H; CH-OSO); anti 5.77 (s, 2H; CH-OSO); 2.33 ppm (s, 6H; Ar-CH\(_{3}\)).

Found: C, 67.2; H, 5.6; S, 11.1. C\(_{16}\)H\(_{16}\)SO\(_{3}\) requires: C, 66.6; H, 5.7; S, 11.0.
meso-3,1-Dichlorohydrobenzoin cyclic sulphite (96)

m. 75°-81°; ν max 1200, 980, 710 cm⁻¹; NMR δ 7.3-6.7 (8H; Ar-H); syn 6.13 (d, 2H; CH-OSO); anti 5.83 (s, 2H; CH-OSO).

Found: C, 51.0; H, 3.3; Cl, 21.7; S, 9.5; C₁₄H₁₀O₇S₂Cl₂ requires: C, 51.1; H, 3.1; Cl, 21.5; S, 14.6.

Reaction of the dimethoxyhydrobenzoin (91) with SOCl₂
by the procedures outlined produced only a crystalline
compound identified as meso-stilbene dichloride (98) m. 134°-135°;
ν max 1612, 1254, 1242, 1170, 1030, 850 cm⁻¹; NMR δ 7.35 (d, J₈Hz, 4H; Ar-H); 6.87 (a, J₈Hz, 4H; Ar-H); 5.18 (s, 2H; CH-Cl);
3.80 ppm (s, 6H; Ar-OCH₃). Found: C, 62.0; H, 5.2; Cl, 22.9.
C₁₆H₁₀O₂Cl₂ requires: C, 61.7; H, 5.2; Cl, 22.8.

Pyrolysis of the cyclic sulphites.

The pyrolyses were carried out by heating the sulphites
(0.07-0.2g) to 250-280° under a stream of nitrogen until
SO₂ ceased to be evolved. The product was taken into
Et₂O and washed free of SO₂ before being analysed. The
carbonyl products identified constituted ca 80-85% of the
pyrolysis mixture.

The yield from the hydrobenzoin cyclic sulphites was
calculated from the NMR spectra by comparing the total
aromatic proton integral, to the integral of the methylene
and methine protons in the ketone and aldehyde respectively. The yield from the alicyclic diol cyclic sulphites was calculated by using trans-4-tert-butylcyclohexanol as a GLC standard. The product ratios were obtained by GLC using a Kent Chromalog digital integrator, and were reproducible to ± 6%. The hydrobenzoin sulphite pyrolysis products were analysed on the SE30 column, and the products from the cyclohexane diol sulphites on the PEGA column. The products were identified by injection with authentic samples prepared independently, or isolated by preparative GLC. The products isolated by preparative GLC are listed below with the column used given in brackets.

Desoxybenzoin\(^7\)(99; SE30); \(^\circ\) max 1695, 1190, 990, 760 cm\(^{-1}\);
NMR \(\delta\) 7.9-9.2(2H; Ar-H); 7.2-7.6(6H; Ar-H); 4.27 ppm
(s, 2H; CO-CH\(_3\)).

Dipheylacetaldehyde\(^7\)(102; SE30); \(^\circ\) max 2840, 2750, 1730, 750, 710 cm\(^{-1}\);
NMR \(\delta\) 9.30(d, J2Hz, 1H; CH-CHO);
7.1-7.6(10H; Ar-H) 4.88 ppm(d, J2Hz, 1H; CH-CHO).

4,4'-Dimethyldesoxybenzoin\(^5\)(100; SE30); \(^\circ\) max 1685, 1180, 825 cm\(^{-1}\);
NMR \(\delta\) 7.90(d, J8Hz, 2H; Ar-H); 7.27(d, J8Hz, 2H; Ar-H); 7.27(s, 4H; Ar-H); 4.22(s, 2H; CO-CH\(_3\)); 2.38
(s, 3H; Ar-CH₃); 2.32 ppm (s, 3H; Ar-CH₃).

Di-p-tolyacetaldehyde (103; SE30); ν max 2840, 2740, 1727, 1024, 820 cm⁻¹; NMR δ 9.78 (d, J2Hz, 1H; CH-CHO); 7.14 (s, 5H; Ar-H); 4.80 (d, J2Hz, 1H; CH-CHO); 2.33 ppm (s, 3H; Ar-CH₃). Found: C, 86.0; H, 7.2. C₁₆H₁₆O requires: C, 85.7; H, 7.2.

3,3'-Dichlorodesoxybenzoin (101; SE30); ν max 1685, 1678, 895, 745 cm⁻¹; NMR δ 7.1-8.0 (8H; Ar-H); 4.22 (s, 2H; CO-CH). Found: C, 63.3; H, 4.1; Cl, 26.4. C₁₄H₁₀OCl₂ requires: C, 63.4; H, 3.8; Cl, 26.8.

3,3'-Dichlorophenyl-acetaldehyde (104; SE30) was not isolated pure, but identified as a mixture with the ketone (101). ν max 2720, 2820, 1727 cm⁻¹; NMR δ 9.87 (d, J2Hz, 1H; CH-CHO); 4.80 ppm (d, J2Hz, 1H; CH-CHO).

3-tert-Butylcyclopentane aldehyde (79; FFAP); ν max 2810, 2710, 1725 cm⁻¹; NMR δ 9.45 (d, J2Hz, 1H; CH-CHO); 0.87 (s, 9H; tert-buty1); 1.2-2.1 ppm (methylenne groups). Mass measurement of ion at 154. Meas: 154.135895. C₁₀H₁₈O requires: 154.135758 (diff. 4 ppm).

3-tert-Butyl-1-methylcyclopentane aldehyde (80; FFAP); ν max 2805, 2700, 1730, 1220, 940, 880 cm⁻¹; NMR δ 9.45
(9, 1H; C-CH4); 1.13(9, 3H; -CH3); 0.87(9, 9H; tert-butyl); 1.0-2.1 ppm(methylene groups). Mass measurement of ion at 168. Meas: 168.150905. C_{11}H_{20}O requires: 168.151467 (diff. 3 ppm).

3-tert-Butylcyclopentane methyl ketone(81; FFAP);
\( \lambda \text{max} 1715, 1350, 1230, 1160 \text{ cm}^{-1}; \) NMR \( \delta 2.15(9, 3H; \text{CO-CH}_3) 0.85(9, 9H; \text{tert-butyl}); 0.9-2.1 \text{ ppm(methylene groups). Mass measurement of peak at 168. Meas: 168.151052. C}_{11}H_{20}O requires: 168.151467(\text{diff. 2 ppm}).

3-tert-Butyl-1-methylcyclopentane methyl ketone(82; FFAP);
\( \lambda \text{max} 1710, 1350, 1340, 1240, 1110 \text{ cm}^{-1}; \) NMR \( \delta 2.13 (9, 3H; \text{CO-CH}_3); 1.20(9, 3H; -CH_3); 0.85(9, 9H; \text{tert-butyl}); 1.1-2.2 \text{ ppm(methylene groups). Mass measurement of peak at 182. Measured 182.167920. C}_{12}H_{22}O requires: 182.167056 (diff. 4 ppm).

\text{cis- and trans-But-2-ene}^{52}(27).

A mixture of butan-1-ol(666g) and H_{2}SO_{4}(60\%, 1500ml) was heated under reflux and the cis- and trans-but-2-ene passed successively through a solution of NaOH(3M), H_{2}SO_{4}(50-55%), dried over CaCl_{2} and condensed in an ampoule at -15 to -20°.
d,l-erythro-3-chlorobutan-2-ol and d,l-threo-3-chlorobutan-2-ol (105).

cis and trans-But-2-ene (132 g) was added to a mixture of HTH (294 g, 65% available chlorine) and ice-water (400-500 g) at -10° to -15°. HAc (175 ml) was then added with vigorous stirring over 2-3 hours. Isolation by means of Et₂O and distillation gave a mixture of d,l-2,3-dichlorobutane and meso-2,3-dichlorobutane (11g, 4%) b₂₀ 50°-60° (Lit. b₈₀ 50°-60°) followed by a mixture of d,l-erythro-3-chlorobutan-2-ol and d,l-threo-3-chlorobutan-2-ol (106 g, 40%) b₃₀ 50°-60° (Lit. b₈₀ 50°-60°; n₀ 20 1.4374; NMR δ 3.95 (Wh/2 25 Hs; H₂ and H₃); 3.22 (0-H)); major signals at 1.50, 1.40 and minor signals at 1.53, 1.43 (J 6 Hz; C₃-H₃); 1.21 ppm (J 6 Hz; C₂-H₃).

cis and trans-2,3-Epoxybutanes (106 and 107).

A mixture of dl-erythro and d,l-threo-3-chlorobutan-2-ol (193 g) was added to a solution of KOH (450 g) in water (250 ml) over 2 hours at 90° with stirring. A slow stream of nitrogen was passed through the system after complete reaction to carry over any remaining epoxide. The product was dried over anhydrous K₂CO₃ and distilled to give GLC pure (Carbowax 20M) 2,3-epoxybutane (67.0 g, 50%) consisting of a mixture (7:3) of trans- (107) and cis-2,3-epoxybutane (108).
Distillation through a spinning band gave GLC pure 
(Carbowax 20M) trans-2,3-epoxybutane (107.38g) b\(_{168}^{53-54}°\)
(Lit.\(_{52}^{52}\) b\(_{16}^{74-53.6}°-54.1°\))  
NMR δ 2.44 (Wh/2 7Hz, 2H; H2 and H3); 1.16 ppm(d, J4Hz, 3H; -CH\(_3\)).

Continued distillation gave pure cis-2,3-epoxybutane (106.18g) 
b\(_{748}^{60-61}°\) (Lit.\(_{52}^{52}\) b\(_{74}^{759.9}°-60.4°\));  
NMR δ 2.76(Wh/2 10Hz, 2H; H2 and H3); major signals at 1.19, 1.10 minor signals at 1.17, 1.13 ppm(J4Hz; C2-H\(_3\), and C3-H\(_3\)).

dL- and meso-Butene-2,3-diol (109 and 108),

Technical dL- and meso-butene-2,3-diol (109 and 108, 1:1) 
was fractionated through a spinning band to give the dL- and 
meso- isomers GLC pure (Carbowax 20M).

dL-Butene-2,3-diol (109) b\(_{168}^{65-86}°\) (Lit.\(_{52}^{52}\) b\(_{16}^{66}°\));  
NMR δ 3.33(Wh/2 13Hz, 2H; CH\(_2\)-OH); 1.06(d, J5Hz, 6H; CHOH-CH\(_3\)); 2.1 ppm(2H; O-H).

meso-Butene-2,3-diol (108) m.34°-35°, b\(_{168}^{66-69}°\) 
(Lit.\(_{52}^{52}\) m.34.4°, b\(_{16}^{68}°\));  
NMR δ 3.69(Wh/2 10Hz, 2H; CH\(_2\)-OH);  
1.07(d, J6Hz, 6H; CHOH-CH\(_3\)); 2.0 ppm(2H; O-H).

trans-Cyclohexene-1,2-diol (110).

Cyclohexene was oxidized with formic acid-H\(_2\)O\(_2\) by the
procedure already described. The product was purified by crystallisation from pentane.

trans-Cyclohexane-1,2-diol(110) m. 102-103°C (Lit. 102-104°C);
λmax 3350, 1065, 1075, 1045, 930 cm⁻¹; NMR δ 3.35 (WH/213Hz, 2H; CH₂-OH); 4.0 (2H; O-H); 0.9-2.2 ppm (8H; methylene groups).

cis-Cyclohexane-1,2-diol(110).

Cyclohexene was oxidized with KMnO₄ by the procedure already described. The product was purified by crystallization from pentane.

cis-Cyclohexane-1,2-diol(111) m. 96-98°C (Lit. 798°C);
λmax 3300, 1075, 990, 960 cm⁻¹; NMR δ 3.77 (WH/2 11Hz, 2H; CH₂-OH); 3.0 (2H; O-H); 1.0-2.0 ppm (8H; methylene groups).

cis- and trans-2,2-Dimethylcyclohexane-1,3-dioxolane (112 and 113).

To a solution of the cyclohexene diol (0.5g) in acetone (2.5ml) was added BF₃-etherate (0.1ml) and the reaction mixture stirred for 10 minutes. Isolation by means of Et₂O and distillation gave the dioxolane(113).
cis-2,2-Dimethylcyclohexane-1,3-dioxolane (113, 0.3\% 50\%)

$\delta$ max 1550, 1370, 1235, 1210, 1045, 1033 cm$^{-1}$; NMR $\delta$ 4.67 (Me/2 2H, 2H; C H-CH$_3$) 1.48 (s, 6H, -CH$_3$); 1.32 (8, 3H, -CH$_3$); 1.0-2.0 ppm (methylene groups). Found: C, 69.1; H, 10.2.

C$_9$H$_{16}$O$_2$ requires: C, 69.2; H, 10.3.

trans-2,2-Dimethylcyclohexane-1,3-dioxolane (112, 0.3\% 50\%)

$\delta$ max 1457, 1225, 1115, 1065, 840 cm$^{-1}$; NMR $\delta$ 3.27 (Me/2 17H, 2H; C H-CH$_3$) 1.4 (s, 6H, -CH$_3$); 1.0-2.0 ppm (methylene groups).

Found: C, 69.3; H, 10.2. C$_9$H$_{16}$O$_2$ requires: C, 69.2; H, 10.3.

**BF$_3$-etherate catalysed reaction of cyclohexene oxide with acetone.**

To a solution of cyclohexene oxide (0.5g) in acetone (2.5ml) at 0\(^\circ\), was added BF$_3$ (0.1ml) and the reaction mixture stirred for 5 minutes. The product was isolated by extraction with Et$_2$O and identified, by comparison with authentic samples of the cis- (113) and trans (112)-dioxolane, as trans-2,2-dimethylcyclohexane-1,3-dioxolane.

**cis-2,2,45-Tetramethyl-1,3-dioxolane (114).**

To a solution of meso-butane-2,3-diol (6.8g) in acetone (2.9g) was added H$_2$SO$_4$ (50\%; 0.2ml) and the solution heated under reflux for 3 hours. The cooled reaction mixture
was poured into aqueous \( \text{K}_2\text{CO}_3 \) and the product isolated by means of Et\(_2\)O. Distillation gave the cis-dioxolane (114, 2.2g 30\%)

\[ b_{\text{750}}^{110\text{°}-112\text{°}} \text{, } \gamma \text{ max } 1250, 1220, 1104, 1035, 850 \text{ cm}^{-1}; \]

\text{NMR } \delta 3.93(\text{br }/2 \text{ 15Hz, 2H; CH}-0); 1.32(\text{s, 3H; -C2-CH}_3); \]

1.22 (s, 3H; -C2-CH\(_3\)); 1.05 (d, J6Hz, 3H; C4-CH\(_3\)); 1.03 ppm

(d, J6Hz; C5-CH\(_3\)). Found: C, 64.8; H, 10.7. \( \text{C}_7\text{H}_{14}\text{O}_2 \)

requires: C, 64.6; H, 10.8.

\text{trans-2,2,4,5-Tetramethyl-1,3-dioxolane.}^{53}(115).

The dioxolane (115) prepared from \( d,1\)-butane-2,3-diol had \( b_{\text{750}}^{109\text{°}-112\text{°}} \), \( \gamma \text{ max } 1243, 1214, 1080, 841 \text{ cm}^{-1}; \)

\text{NMR } \delta 3.43(\text{br }/2 \text{ 11.5Hz 2H; CH}-0); 1.27(\text{s, 6H; C2-CH}_3); \]

1.15 (s, 3H; C4-CH\(_3\)); 1.13 ppm (s, 3H; C5-CH\(_3\)).

\text{BF}_3-\text{Catalysed reaction of but-2-ene epoxides with 0}^{18}-\text{labelled acetone.}

(a) \text{cis-Epoxide(dry). To a solution of cis-epoxide (106; 0.05ml) in acetone(3.9\% 0}^{18}; 0.25ml) was added BF}_3-

etherate(0.03ml) and the mixture kept at 0\text{°} for 10 minutes. The reaction mixture was diluted with Et}_2\text{O}(25ml) and washed with water (10x 5ml). Et}_2\text{O was removed from the dried solution by distillation to give trans-dioxolane(115, identified by GIC and NMR.}
(b) cis-Epoxide (wet). Conditions were as for (a) except that water (2.5 ml) was added prior to the BF₃-etherate, and yielded the trans-dioxolane (115).

(c) trans-Epoxide (dry). Reaction conditions, as for (a), converted the trans-epoxide (107) to the cis-dioxolane (114), identified by GLC and NMR.

(d) trans-Epoxide (wet). Conditions were as for (b); trans-epoxide (107) was converted to the cis-dioxolane (114).

BF₃-Catalysed reaction of butane-2,3-diols with 18O

(a) meso-Diol. To a solution of meso-butane-2,3-diol (108; 0.05 ml) in acetone (8.9% O₁₈; 0.25 ml) was added BF₃-etherate (0.01 ml) and the reaction mixture kept at 0°C for 10 minutes. Isolation of the product as for epoxide reactions, gave the cis-dioxolane (114) identified by GLC and NMR.

(b) dl-Diol. Reaction as for (a) using dl-butane-2,3-diol (109) gave the trans-dioxolanes (115) identified by GLC and NMR.
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\[
\begin{array}{c}
\text{Fig. 1} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Fig. 2} \\
\end{array}
\]
ROH + ClSCl → ROSCl + HCl

ROS-Cl + R^1OH → ROSOR^1 + HCl

Fig. 5

Fig. 6

Fig. 7

Fig. 8
Fig. 9

Fig. 10

Fig. 11
\[
\begin{align*}
\text{Na}^+ & \quad \text{O}^\cdot \quad \text{R}^+ \quad \text{H} \quad \text{OR} \quad \text{Na}^+ \\
\text{R}^\cdot \quad \text{C} \quad \text{R}^+ \quad \text{H} \quad \text{OR} \quad \text{Na}^+ \\
\text{R}^\cdot \quad \text{C} \quad \text{R}^+ \quad \text{H} \quad \text{OR} \quad \text{Na}^+ \\
\text{R}^\cdot \quad \text{C} \quad \text{R}^+ \quad \text{H} \quad \text{OR} \quad \text{Na}^+ \\
\end{align*}
\]
Fig. 13
Fig. 14

\[ I_2 + CH_3CO_2Ag^+ \rightarrow CH_3CO_2I + AgI \]

\[ CH_3CO_2I + CH_3CO_2Ag^+ \rightarrow CH_3CO_2I \cdot CH_3CO_2Ag^+ \]

(Simonini Complex)

Fig. 15
% Relative population when

1). \( a = e = H \)

2). \( a = CH_3; \quad e = H \)

3). \( a = H; \quad e = CH_3 \)

Fig. 20
Fig. 21

Ketone Aldehyde

25  70

Observed

Fig. 22

51A

147

100
(i) Fig. 23

rotation followed by ring closure

(i) Fig. 23

H

(iii) Fig. 24

ring closure
Fig. 25
Fig. 26
Fig. 27
Fig. 28.
Fig. 29
Fig. 30
Fig. 31
Fig. 32
$RO-S-OR$

$\text{1}$

$\text{2}$

$\text{3}$

$\text{4}$

$\text{5}$

$\text{6}$

$\text{7}$

$\text{7a}$

$\text{7b}$

$\text{8}$

$\text{8a}$

$\text{8b}$

$\text{8c}$

$\text{8d}$

$R' = \text{CH}_3, R = \text{H} \quad (8a, 8b)_{20}$

$R' = R = \text{CH}_3 \quad (8a, 8c, 8d)_{23}$

$R' = R = \text{C}_6\text{H}_5 \quad (8a, 8d)_{7}$
\[ CH_3CH \equiv CHCH_3 \]

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(Fig. 22)