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PHOTOCHEMICAL REACTIONS OF SELECTED EPOXIDES

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ABSTRACT

The synthesis and photolysis of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1), 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3), 3S(3R)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4), oxiranyl benzoate (25) and 2,3-epoxy-3-methyl-1-butanol benzoate (28) are described and the structures of 1S,2S(1R,2R)- and 1R,2S(1S,2R)- 2-methyl-1-phenyl-3-buten-1-ols (9) and (10), and 1S,2R,3R(1R,2S,3S)-, 1S,2R,3S(1R,2S,3R)-, 1R,2R,3S(1S,2S,3R)- and 1R,2R,3R(1S,2S,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanols (12), (13), (14) and (15) unambiguously determined.

Photolysis of a solution of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1) in benzene gave the isomeric 1S,2S,3S(1R,2R,3R)- and 1R,2S,3S(1S,2R,3R)- 2,3-epoxy-1-phenyl-1-cyclobutanols (30) and (31). The formation of these products is rationalised by a mechanism involving γ -hydrogen abstraction by the excited carbonyl moiety and closure of the resulting 1,4-biradical. Fragmentation of the 1,4-biradical is a less important process and only a trace of acetophenone could be detected. Photolysis of 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanone (2) and (3) gave 1R,2S,3S,4S(1S,2R,3R,4R)- and

1R,2R,3R,4S(1S,2S,3S,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (36) and (35) respectively. The stereospecificity of these reactions is rationalised. Photolysis of 3S(3R)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) gave 3-methyl-2-buten-1-ol benzoate (29), a product resulting from initial α -cleavage. Only a trace of product resulting from γ -hydrogen abstraction could be isolated. Oxiranyl benzoate (25), the C(2) oxygen analogue of 3,4-epoxy-1-phenyl-1-butanone (1), and 2,3-epoxy-3-methyl-1-butanol benzoate (28) were photochemically unreactive, but ground state addition of hydrochloric acid to oxiranyl benzoate (25) was observed when the compound was photolysed with 1849 - 2537 Å ultraviolet lamps in dichloromethane.

The photolysis of 4 α ,5-epoxy-5 α - and 4 β ,5-epoxy-5 β -cholest-2-enes (51) and (52) in acetone to give the skeletal rearrangement products A-nor-B-homo-5 β - and 5 α -cholest-2-en-6-ones (53) and (55) respectively are described. The mechanism proposed for the formation of these products involves initial C(4) - O bond cleavage followed by stereospecific C(5) - C(10) bond migration to C(4).

INTRODUCTION

The availability of photoreactors and suitable ultraviolet lamps in recent years has resulted in intensive investigations of the chemistry of excited organic species. New reactions have been found and old reactions reinvestigated. These studies have contributed to a better understanding of excited state chemistry and new theories have emerged to take account of the subtleties observed.

The photochemical reactions of ketone derivatives, for example, α, β -¹⁻³ and β, γ -⁴⁻⁷ unsaturated ketones, α, β -epoxyketones⁸⁻¹⁰, cyclohexadienones¹¹⁻¹³, 1-alkoxy-1-phenylalkyl phenyl ketones¹⁴ and 1-phenyl alkyl phenyl ketones¹⁵ have been extensively studied¹⁶. These compounds absorb light in the ultraviolet region of the spectrum (150 - 320 nm) which results in the promotion of an electron from an n or π orbital to a π^* orbital (i.e., $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ excitation). The $n \rightarrow \pi^*$ process is illustrated in Figure I.¹⁷ When the spins of the unpaired electrons are anti-parallel the excited state is referred to as a 'singlet' and when the spins of the unpaired electrons are parallel the excited state is referred to as the 'triplet'. An excited singlet state species can lose energy by collisional transfer, a process referred to as

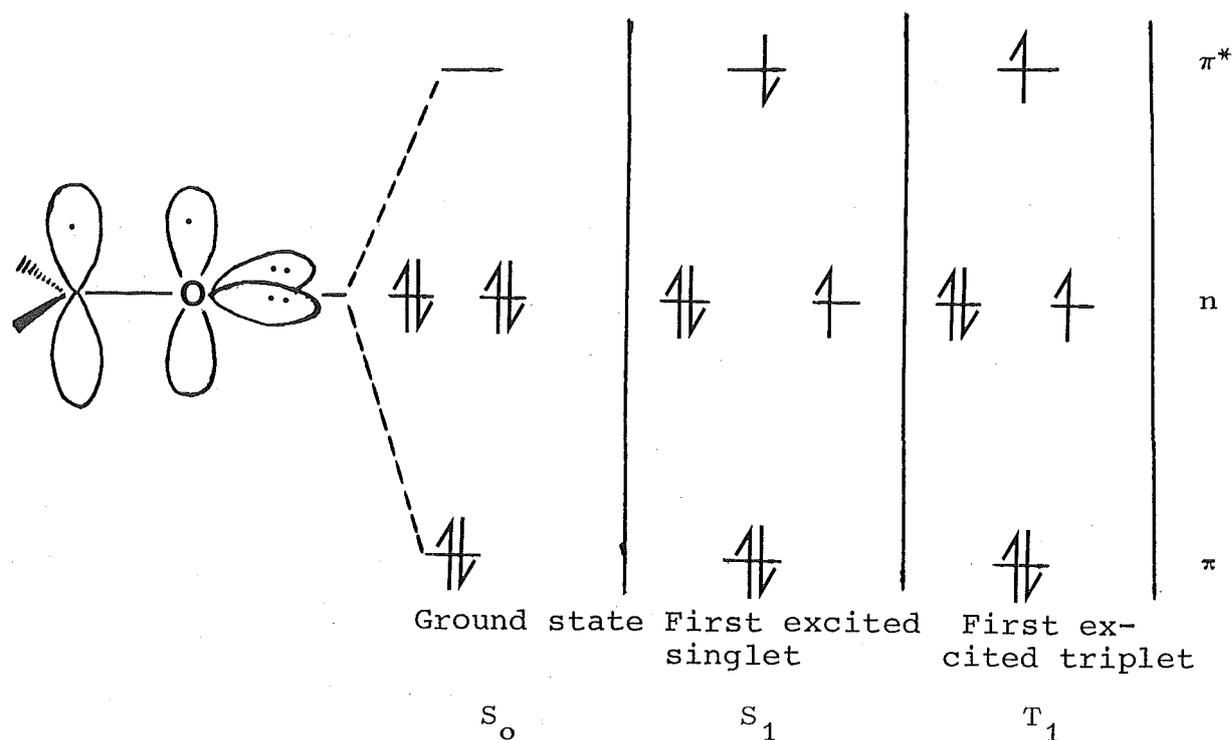
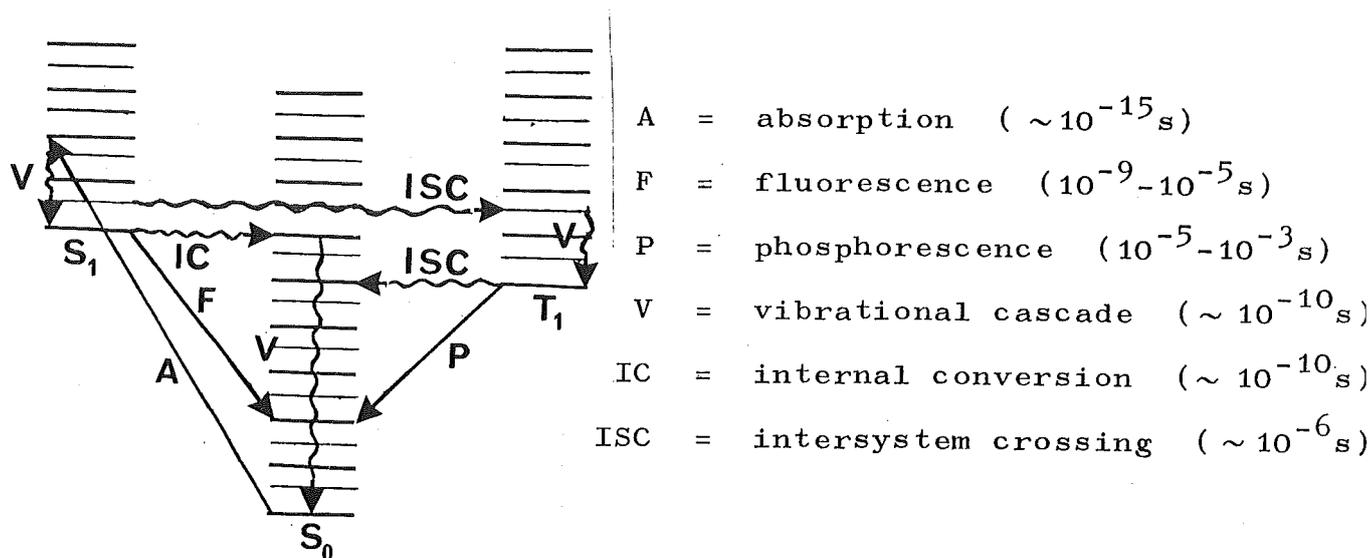


Figure I

vibrational cascade, or by radiative deactivation. It can also undergo intersystem crossing to a triplet state, internal conversion or fluorescence to an excited level of the singlet ground state, or undergo chemical change. These processes are shown in the following Jablonski diagram¹⁸ (Figure II¹⁷). The molecule in an excited triplet state (say T_1) may lose energy by phosphorescence, undergo chemical reaction, cross to an excited level of the singlet ground state (ISC) or dissipate energy by collision with a triplet quencher (e.g. naphthalene or dienes). Photoreaction of aromatic ketones almost always involves excited triplet states¹⁹. Often both singlet and triplet excited states are responsible for photoreactions of



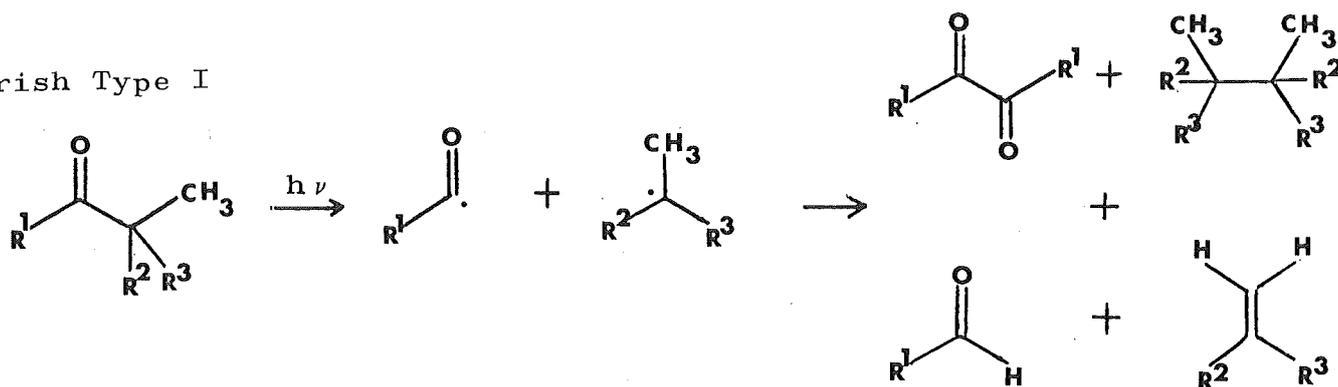
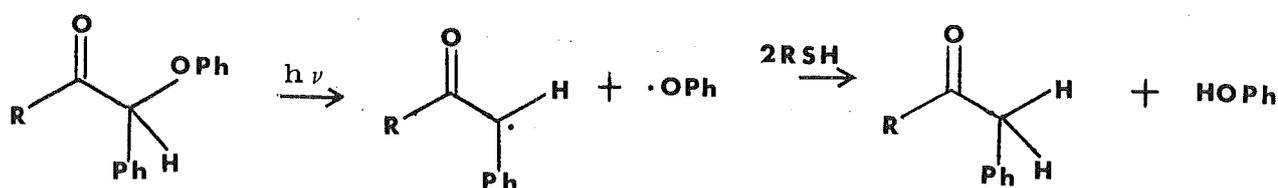
Jablonski Diagram

Figure II

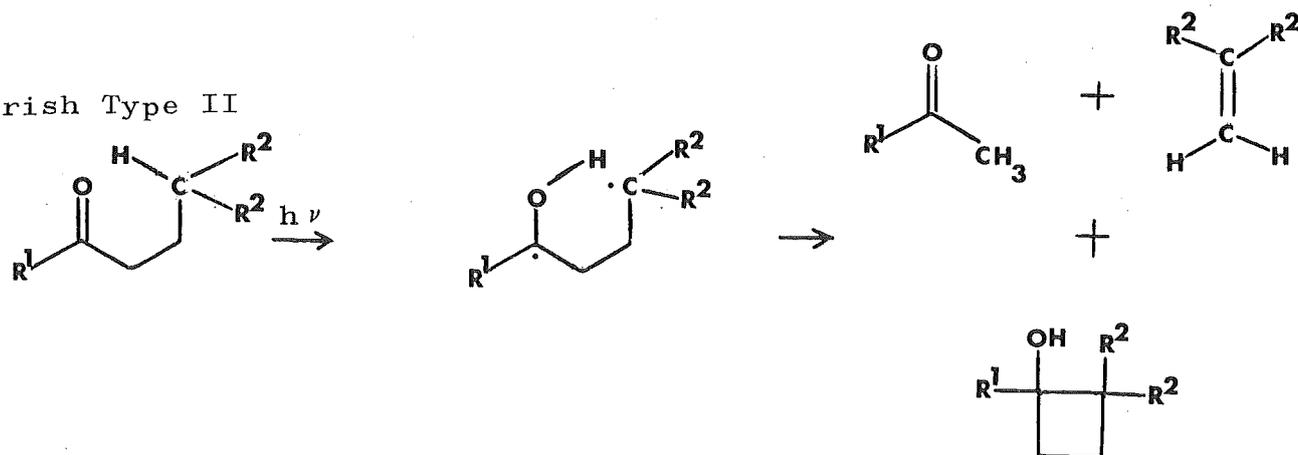
aliphatic ketones. Intersystem crossing for aliphatic ketones is less efficient than for aromatic ketones. The triplet state for aliphatic ketones can often however be obtained by use of triplet sensitizers.

Carbonyl compounds on photolysis give a wide range of products and some of the possible reaction routes of particular interest to this investigation are illustrated in Scheme I. α -Bond cleavage, often referred to as a Norrish Type I photoprocess, frequently occurs in aliphatic and aromatic ketones, and results in two radical fragments which can undergo fragmentation, combination, disproportionation or radical substitution. For example, photolysis³⁴ of 2,2,4,4-tetramethyl-3-pentanone gives 2-methylpropane, 2-methylpropene, 2,2,3,3-tetramethylbutane and carbon monoxide. α -Cleavage is generally biased

Norrish Type I

 β -Cleavage

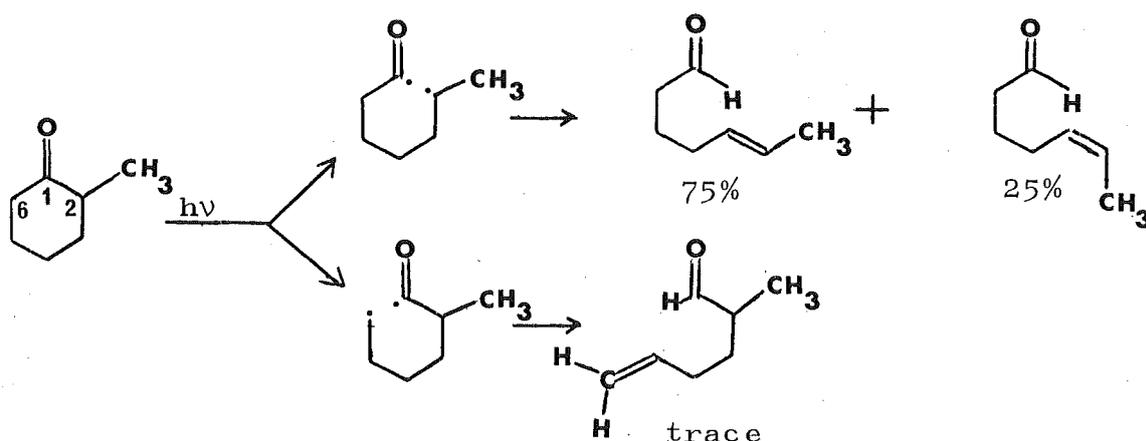
Norrish Type II



Scheme I

towards rupture of the more substituted bond. For example 2-methylcyclohexanone³⁵ gives a mixture of the trans- and cis-5-heptenal formed via C(1)-C(2) bond cleavage and only a trace of 2-methyl-5-hexenal

formed via C(1)-C(6) bond cleavage (Scheme II). Cleavage of the C(1)-C(2) bond is favoured by a factor of at least fifty over C(1)-C(6) bond cleavage in line with the expected relative stability of the different intermediate biradicals (Scheme II).

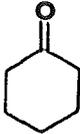
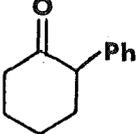
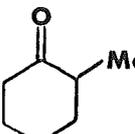
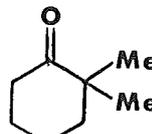


Scheme II

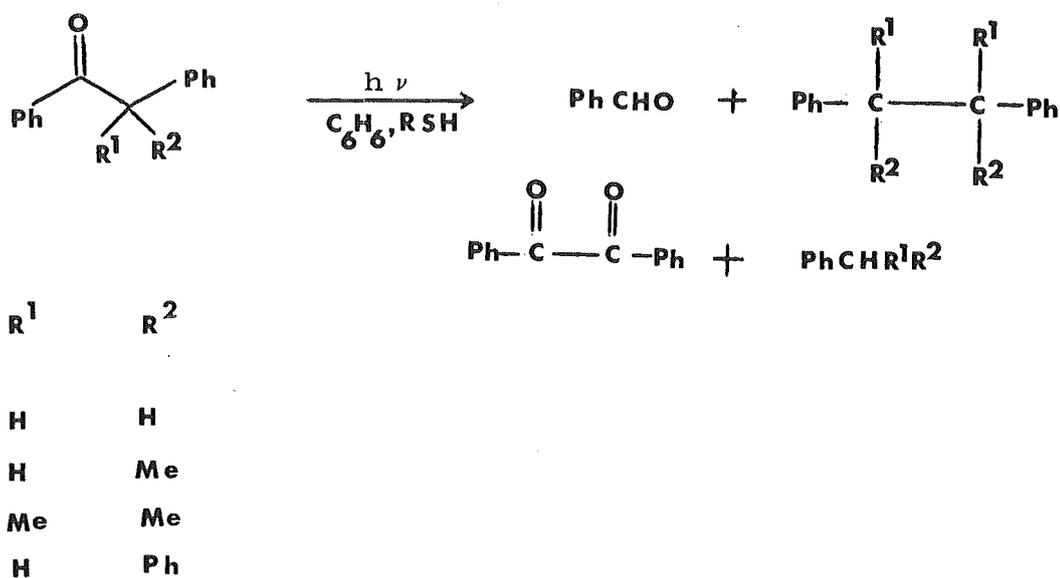
Photolysis of some substituted cyclohexanones³⁶ (Table I) however occurs in a manner which is not consistent with stability of the intermediate biradicals being a major controlling factor in determining which bond is cleaved. If radical stability was important, 2-phenylcyclohexanone would be expected to be the most reactive member of the series of compounds shown in Table I, but the rate of α -cleavage for this compound is approximately five times slower than for the dimethyl compound and comparable to the monomethyl derivative.

From a study of the photochemistry of 1-phenylalkyl phenyl ketones which undergo exclusive α -cleavage

Table I Rates of α -cleavage for some C(2)-
substituted cyclohexanones

Compound				
Rate of α -cleavage ($k_{\alpha} \times 10^8 \text{ sec}^{-1}$)	0.33	3.3	4.7	18.7

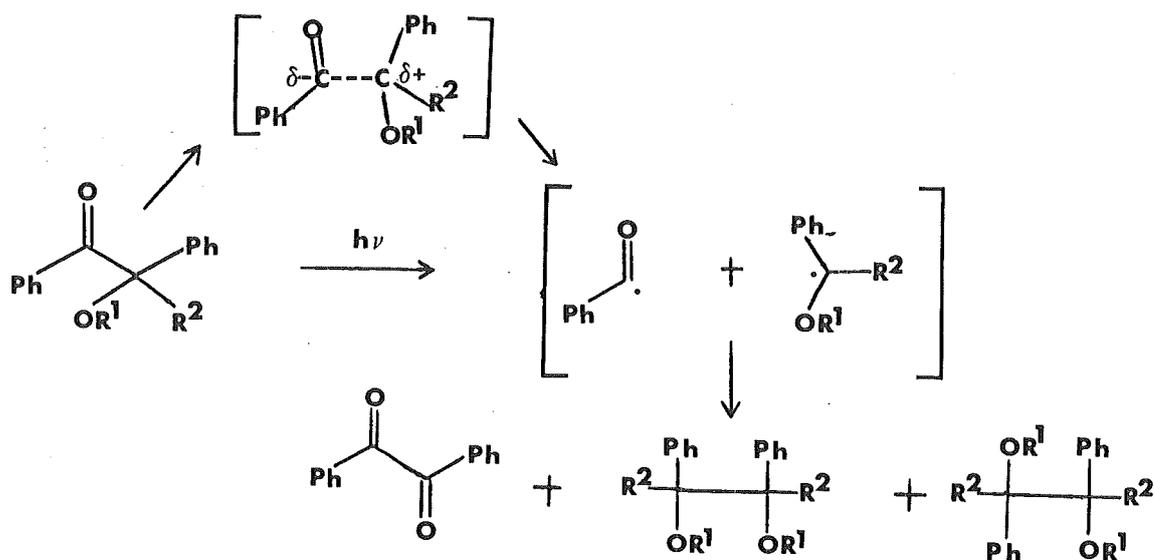
(Scheme III), Heine et al.¹⁵ have also suggested that radical stability is unimportant in determining the



Scheme III

rate of reaction. From bond dissociation studies³⁷, α -cleavage of these compounds would be expected to be exothermic and therefore the transition states should be more like the excited states of the starting ketones than the radical intermediates. They conclude that the increased reactivity toward α -cleavage with increasing alkyl and aryl substitution at C(2) is due to ground state steric effects.

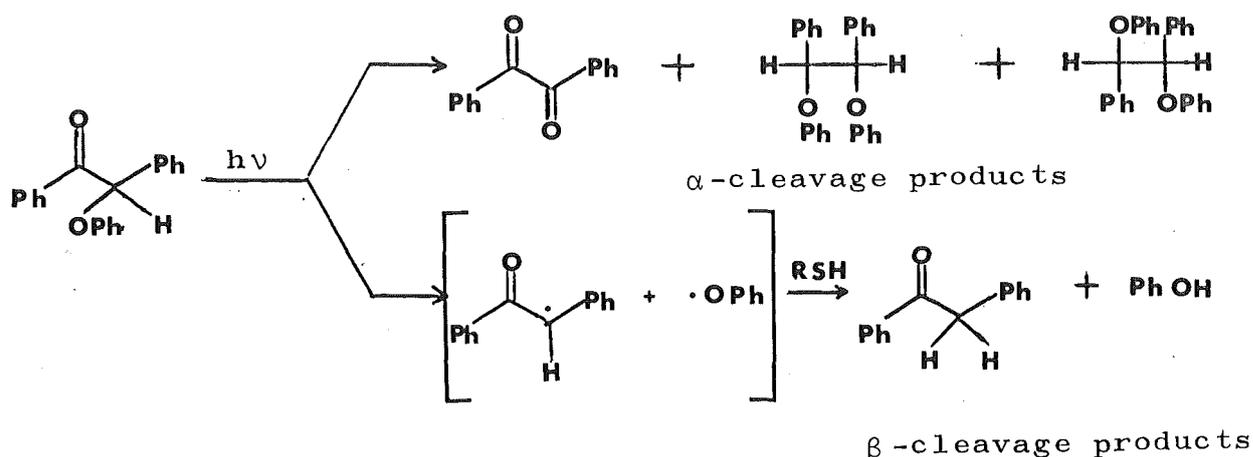
The nature of the transition state for α -cleavage is still a matter of debate. From studies on 1-alkoxy-1-phenylalkyl phenylketones¹⁴ (Scheme IV) the



Scheme IV

suggestion has been made that the transition state for bond cleavage has considerable ionic character. Substituents on the ether oxygen capable of stabilising a

positively charged centre are more effective in accelerating α -cleavage than are substituents capable of stabilising a free radical centre. The negative charge on the carbonyl compound is in keeping with the known polarity of an excited carbonyl moiety. Although substituents at the α -carbon have little effect on the efficiency of α -cleavage, they have a pronounced effect on the rate of cleavage. For instance, alkoxyphenylmethyl phenyl ketones¹⁴ are about 10^5 times more reactive toward α -cleavage than benzyl phenyl ketones. Photolysis of phenoxyphenylmethyl phenyl ketone in benzene in the presence of dodecanethiol (RSH) gave in addition to benzaldehyde, diphenyl diketone, and pinacol ethers, small amounts of phenol and benzyl phenyl ketone which arise from β -cleavage (Scheme V).

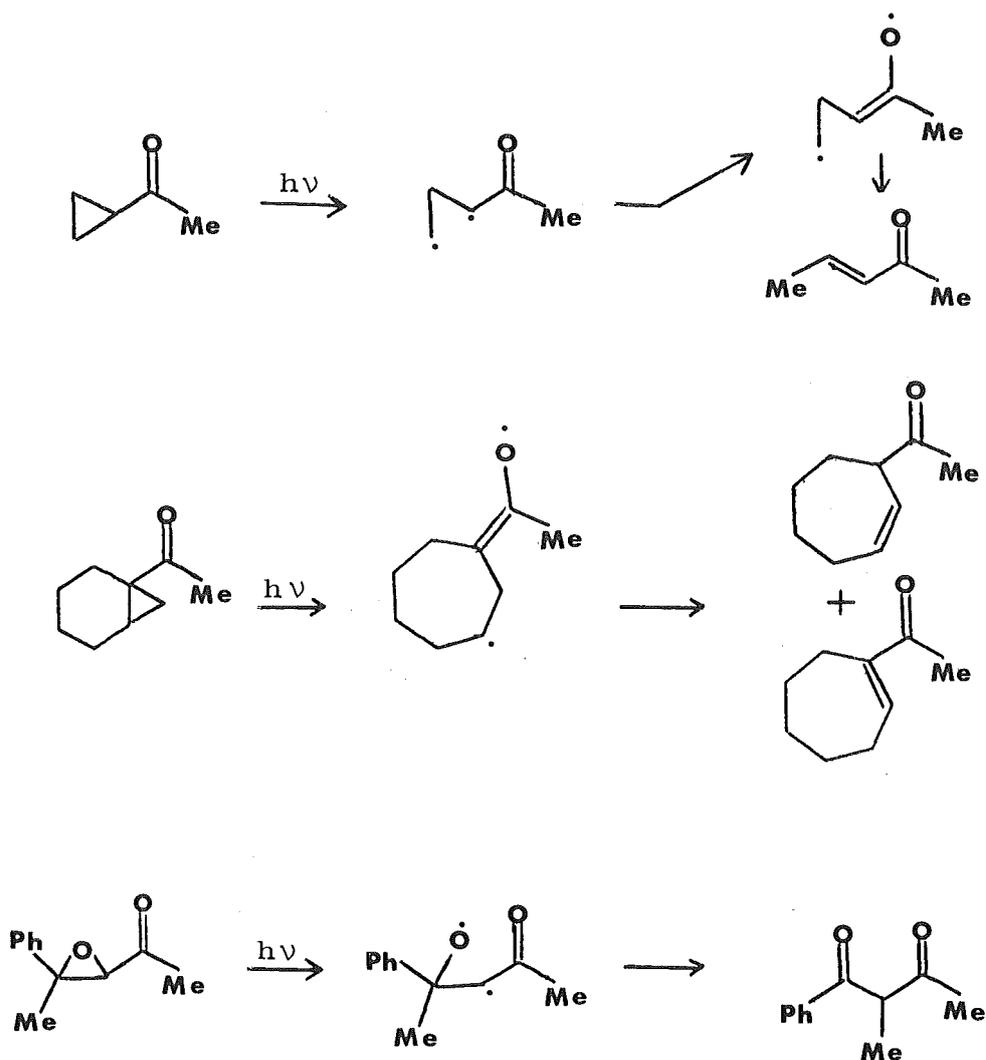


RSH- dodecanethiol

Scheme V

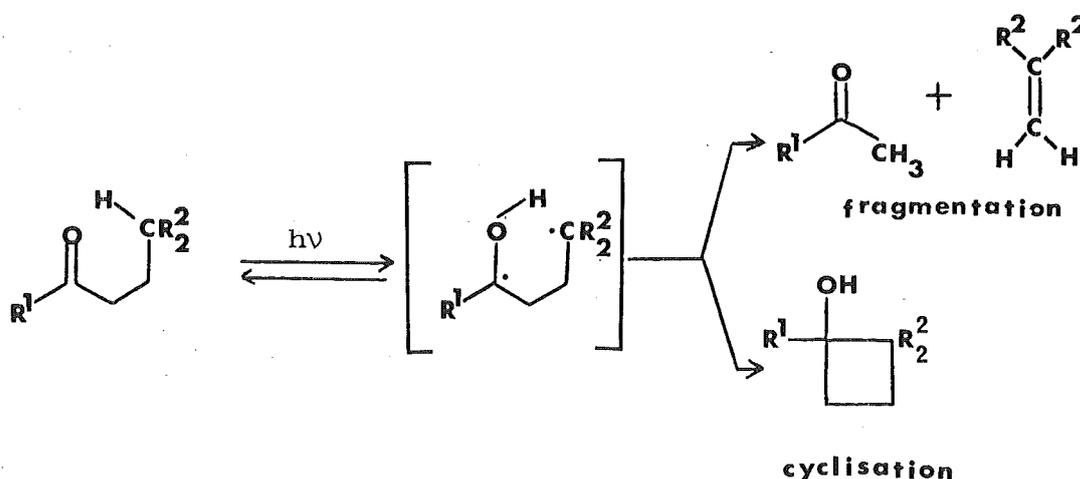
The quantum yields for the formation of benzaldehyde, an α -cleavage product, ($\phi = 0.39$), and phenol, a β -cleavage product, ($\phi = 0.12$), are biased in favour of α -cleavage by a factor of three.

Examples of β -cleavage in excited state reactions of ketones are well documented^{10,38,39}. Often β -cleavage is only a minor pathway but for photo-reactions of small ring carbonyl compounds such as the cyclopropyl methyl ketones⁴⁰ and 3,4-epoxy-4-phenyl-2-pentanone¹⁰ shown in Scheme VI, this process is important.



Scheme VI

In addition to α - and β -cleavage, ketones which contain a γ -hydrogen can undergo 1,5-intramolecular hydrogen abstraction⁴¹⁻⁴³. This is known as a Norrish Type II reaction and results in the formation of a highly reactive 1,4-biradical. This biradical may undergo cyclisation, fragmentation or reverse hydrogen abstraction and these processes are shown in Scheme VII.



Scheme VII

Evidence for intramolecular γ -hydrogen transfer was obtained by Coulson et al.⁴⁴ who detected acetone- d_1 in the photolysis of 2-hexanone-5,5- d_2 . The rate of γ -hydrogen abstraction has been measured for a series of substituted alkyl phenyl ketones of general formula $Ph-\overset{O}{\underset{H}{\parallel}}C-CH_2-CH_2-CHR^1R^2$ and shown to be dependent on the $C(\gamma)-H$ bond strength⁴¹ (Table II).

R ¹	R ²	Φ_{II}^{α}	$10^{-8} k_{\gamma} \text{ sec}^{-1}$
H	H	0.36	0.08
CH ₃	H	0.33	1.3
CH ₃	CH ₃	0.25	4.8
C(CH ₃) ₃	H	0.24	2.0
C ₆ H ₅	H	0.50	4.2
CH ₂ =CH-	H	0.26	5.0

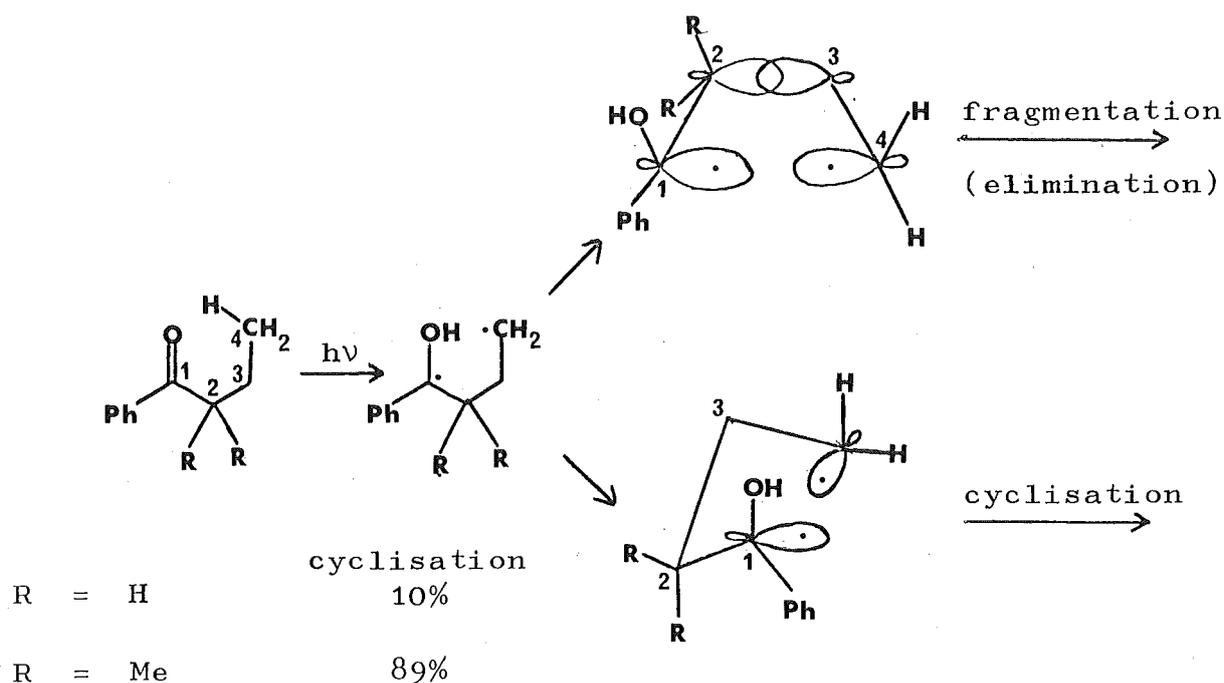
Table II

The measurements taken on a 0.10 M solution of ketone in benzene with 3130 Å irradiation, precision ± 0.01 .

A comparison of the first three entries show that the reactivity of primary, secondary and tertiary C-H bonds differs. The tertiary γ -hydrogen is the most readily removed. Allylic and benzylic substituents as well as alkyl substituents on the γ -carbon enhance k_{γ} values.

Lewis et al.^{37,45} from a detailed study on a series of ten alkyl aryl ketones ~~has~~ rationalised the effect of α -substituents on the partitioning of the reactions between cyclisation and fragmentation. A comparison of the photolysis of 2,2-dimethyl-1-phenyl-1-butanone and 1-phenyl-1-butanone⁴⁵ (Scheme VIII) illustrates the effect of α -substituents on the course of the reaction.

In order that the 1,4-biradical may undergo

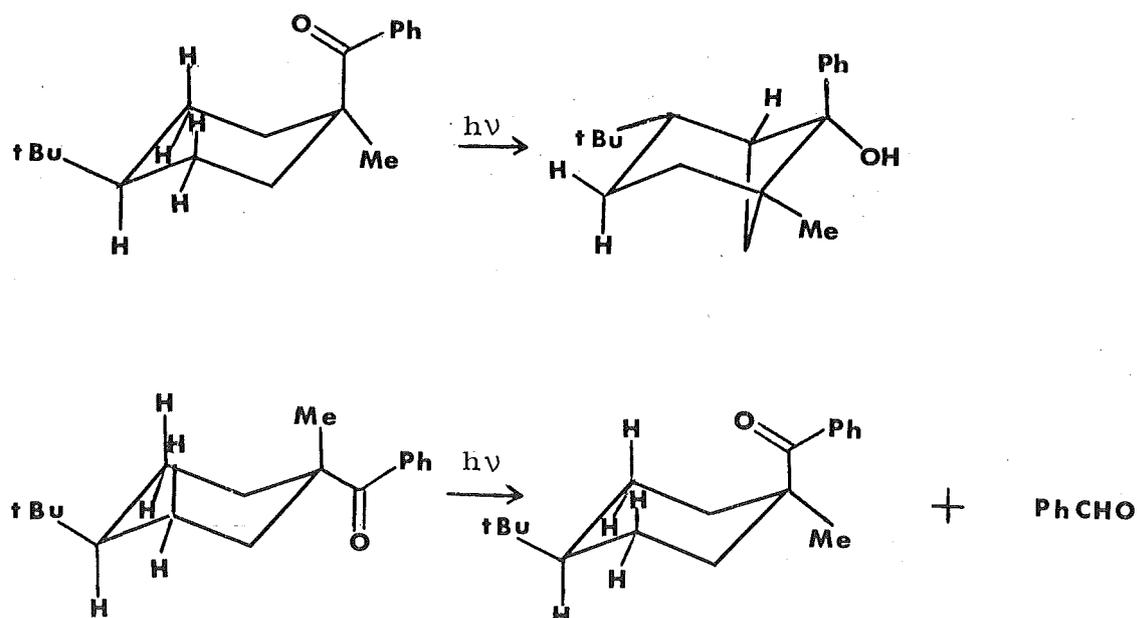


Scheme VIII

elimination, overlap of the C(1) and C(4) radical orbitals with the C(2)-C(3) bond must occur. In such a conformation the substituents at C(2) are eclipsed with the C(1) substituents. This interaction is removed if the biradical assumes the non-planar conformation which allows for overlap of the radical orbitals at C(1) and C(4) without introducing eclipsing interactions. It can be seen therefore that α -substituents will favour cyclisation over elimination and this is found experimentally. β -Substituents have been shown to favour elimination because of the effect of 1,3-diaxial interactions destabilising the transition state for cyclisation. Not all carbonyl compounds with γ -hydrogens however give Type II photoproducts. This may result because rapid reversible hydrogen

abstraction competes with these reactions or the carbonyl may be positioned so as to be incapable of effecting hydrogen abstraction.

Model studies on the 4-tert-butyl-1-methyl cyclohexyl phenyl ketones⁴⁶ shown in Scheme IX revealed

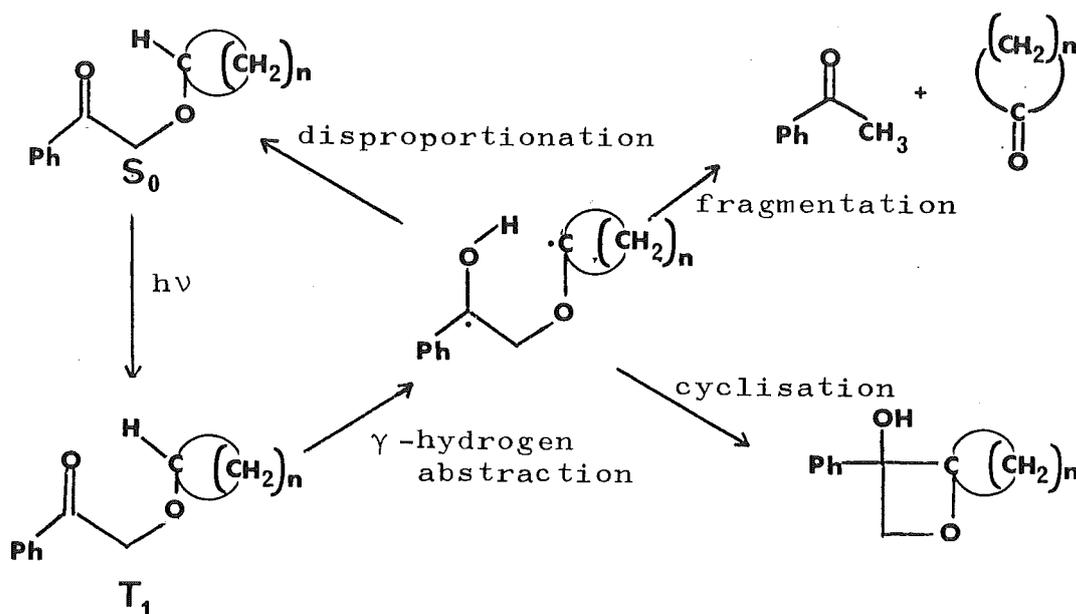


Scheme IX

that while the cis-isomer undergoes Norrish Type II cyclisation, the trans-isomer undergoes α -cleavage to give benzaldehyde and the cis-isomer. The absence of Type II products from the trans-isomer was attributed to the inaccessibility of γ -hydrogens to the excited carbonyl oxygen. α -Cleavage is therefore more rapid than ring inversion to give a conformation where the carbonyl oxygen is positioned to

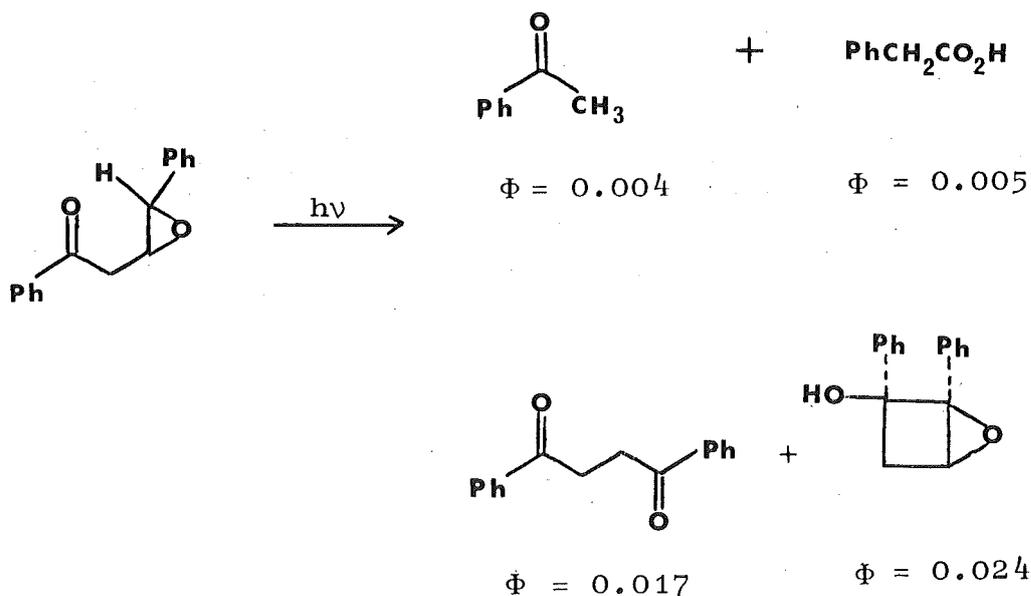
abstract a γ -hydrogen. In contrast 'pseudorotation' in cyclopentyl phenyl ketones⁴⁷ is more rapid than α -cleavage and the product distribution in this case is therefore independent of ground state conformational populations.

As the understanding of the photochemistry of ketones and in particular Norrish Type II reactions has increased, the synthetic utility of these reactions has become more important. Many compounds otherwise unattainable from ground state reactions have been synthesised via Norrish Type II reactions and often in high yields. These include 1-oxaspiro [3.n]-alkanes which were synthesised in high yields from photolysis⁴⁸ of an appropriately substituted α -cycloalkoxyacetophenones (Scheme X). Photolysis of



Scheme X

The photochemical reaction of 3*S*,4*S*(3*R*,4*R*)-1,4-diphenyl-3,4-epoxy-1-butanone with 3000 Å ultraviolet lamps has been studied⁴⁹. The photoproducts and respective quantum yields are shown in Scheme XII. The

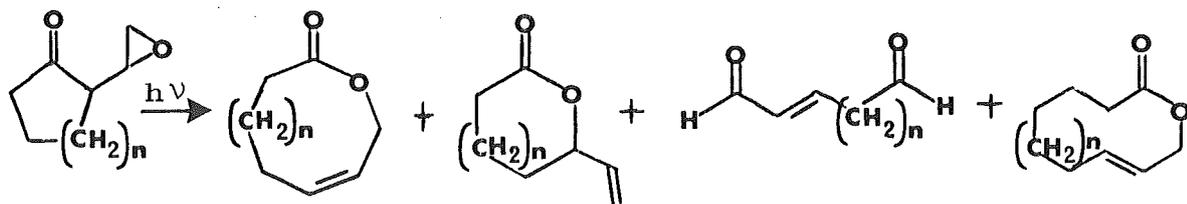


Scheme XII

configuration of the epoxycyclobutanol was determined from the infrared spectrum and should be regarded with caution. The $n \rightarrow \pi^*$ triplet excited state is involved since the reaction is quenched by addition of piperylene. The excited carbonyl abstracts a γ -hydrogen to give a 1,4-biradical. Closure of this biradical gave the

Carlson and co-workers have examined the photo-⁵⁰lysis of some 2-(oxiranyl)cycloalkanones as possible precursors to macrolides. These undergo α -cleavage to give products identified as alkenolides (macrolides), vinyl alkanolides and alkenedials in high yield. Four compounds were studied and the results reported are summarised in Table III. With the possible exception

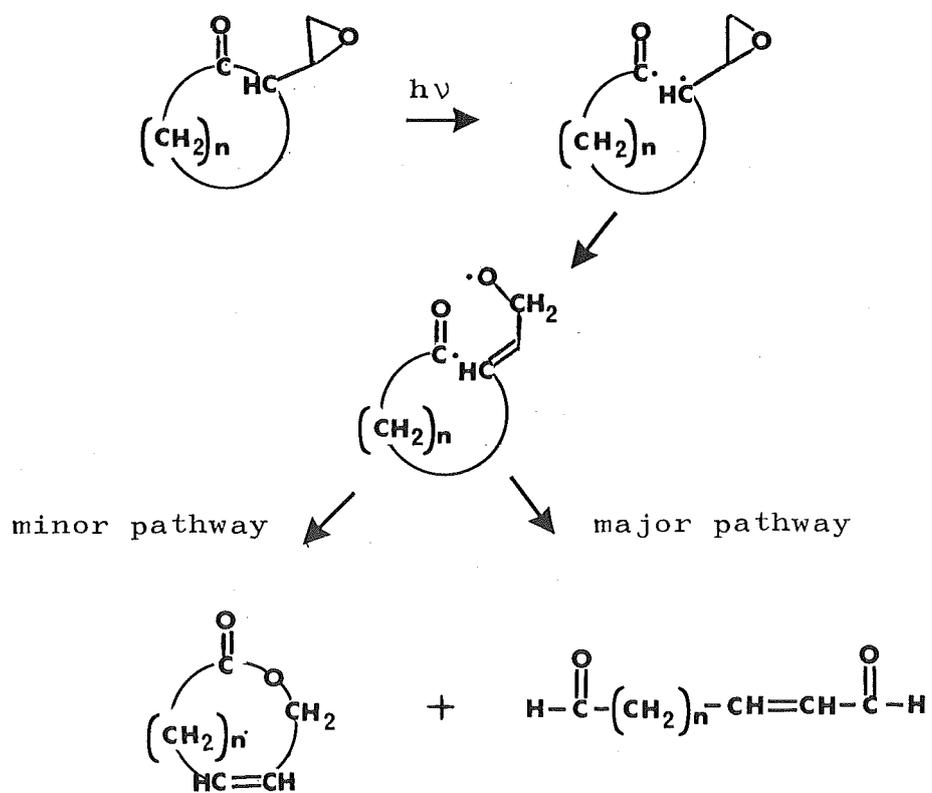
Table III: Photolysis of 2-(oxiranyl)cycloalkanones and product yields.



n = 1	n = 1 (65%)	n = 1 (25%)	n = 3 (8%)	
n = 2	n = 2 (52%)	n = 2 (25%)	n = 4 (24%)	
n = 3	n = 3 (42%)		n = 5 (19%)	n = 1 (26%)
n = 4	n = 4 (50%)		n = 6 (7%)	n = 2 (36%)

of 6-vinyl-1-oxacyclohexan-2-one and 7-vinyl-1-oxacycloheptan-2-one the remaining products are envisaged

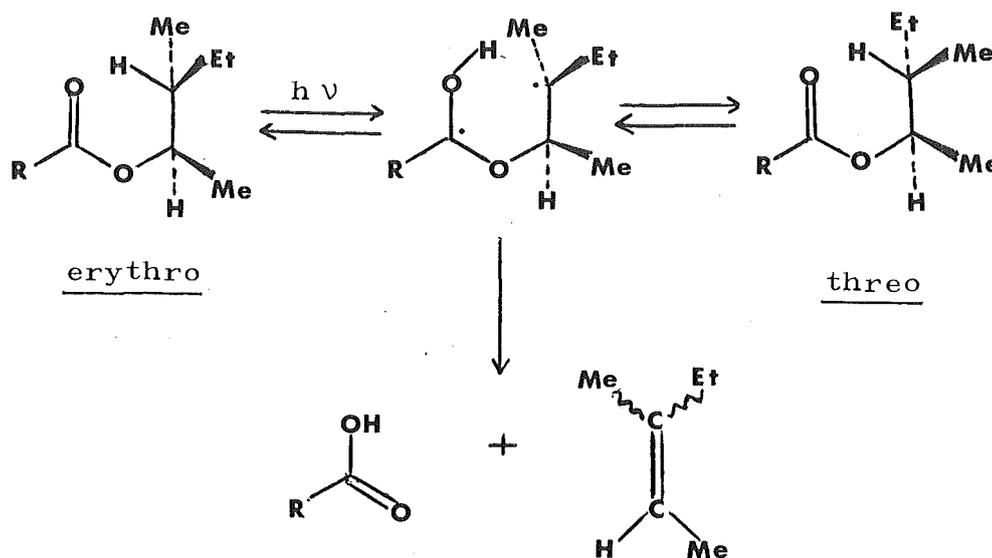
to arise via initial α -cleavage (Scheme XIV).



Z- and E- forms

Scheme XIV

Interest in Norrish Type II photoreactions has mostly centred on aromatic and aliphatic ketones. Intermittent investigations^{51,52} on aromatic esters has left a number of problems to be solved in this area. For esters of general formula $\text{ArCOOCH}_2\text{CH}_2\text{R}$, the Norrish Type II photoelimination to give benzoic acid and olefin derivatives has been shown to be inefficient⁵³ ($\Phi_{\text{ArCOOH}} \approx 0.01$). This lack of apparent reactivity was attributed to a rapid reversible intramolecular γ -hydrogen abstraction of the initially produced 1,4-biradicals competing with product formations. More recently this explanation has been questioned since studies on the photoreactions⁵⁴ of erythro- and threo-1,2-dimethylbutyl-p-methoxybenzoate show that while less than 3% isomerisation occurs benzoic acid is formed in 3-6% yield (Scheme XV).



R = p-methoxyphenyl

Scheme XV

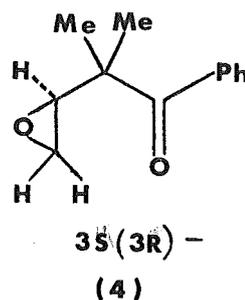
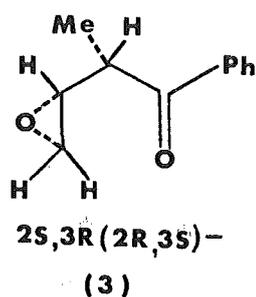
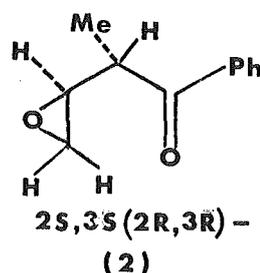
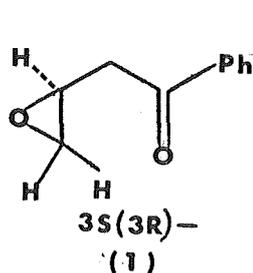
If reversible γ -hydrogen transfer was important in this reaction, the ester should isomerise rapidly since rotation about the C - C bonds is expected to be faster than reverse hydrogen transfer.⁵⁵

This thesis is concerned with the systematic investigation of the photochemical reactions of some acyclic β , γ -epoxycarbonyl compounds. In particular the following compounds have been prepared and their photolysis reactions studied; 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1), 2S,3R(2R,3S)- and 2S,3S(2R,3R)-3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3), 3R(3S)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4), oxiranyl benzoate (25) and 2,3-epoxy-3-methyl-1-butanol benzoate (28).

DISCUSSION

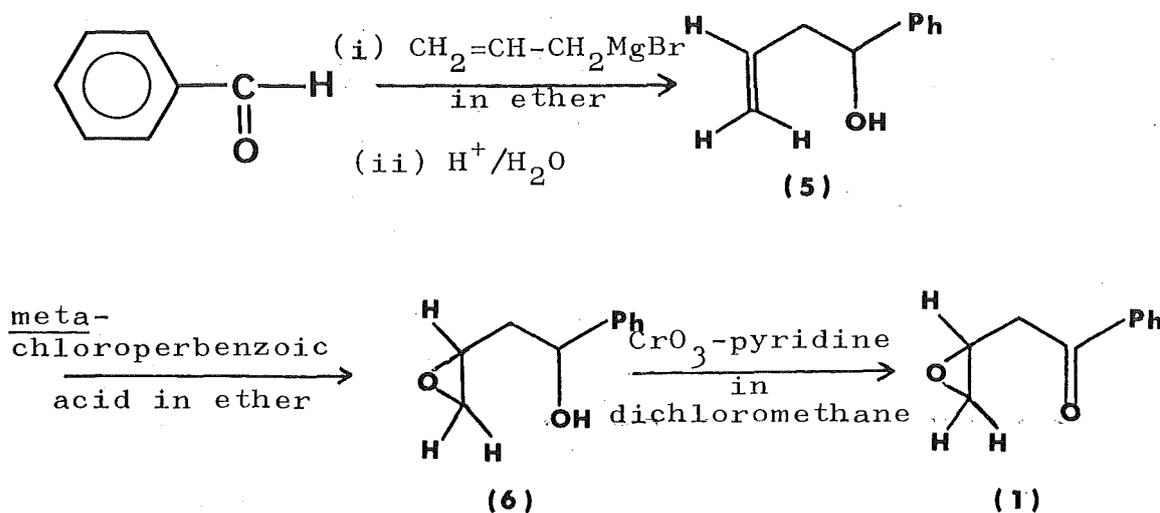
Synthesis

The synthetic pathway chosen to prepare 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1), 2S,3S(2R,3R)- and 2S,3R(2R,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3) and 3S(3R)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) which were required for the photolysis studies involved reaction of an



appropriate organo-magnesium Grignard reagent with ^{56,57} benzaldehyde. Epoxidation of the resulting hydroxy-alkenes followed by oxidation to the ketones gave the required substrates. The synthetic scheme for

the preparation of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1) is shown in Scheme XVI.



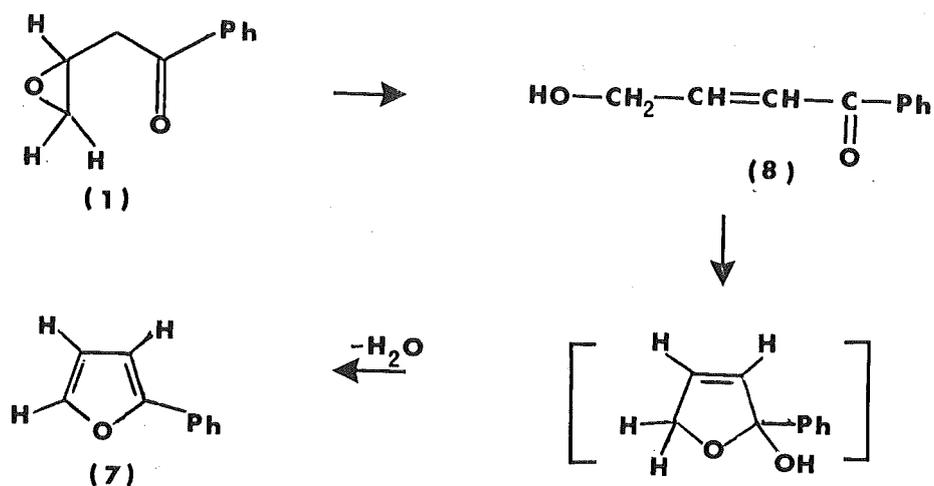
Scheme XVI

The pmr spectrum of 1S(1R)-1-phenyl-3-buten-1-ol (5)⁵⁸ showed a singlet at δ 2.40, identified as the hydroxyl proton by exchange with D_2O . The C(2) methylene protons appeared as a doublet of doublets (J 6.5 Hz, J' 6.5 Hz) centred at δ 2.55. These protons were coupled with C(1)H, which appeared as a triplet (J 6.5 Hz) centred at δ 4.73, and with the C(3)H. The three olefinic protons were a complex multiplet between δ 4.85 - δ 6.18. The aromatic protons were observed as a multiplet centred at δ 7.32. The infrared spectrum of this alcohol (5) further confirmed the presence of hydroxyl (3425 cm^{-1}), olefinic ($926, 1458, 1498\text{ cm}^{-1}$) and aromatic ($765, 707\text{ cm}^{-1}$) functions. An absorption characteristic of a monosubstituted aromatic chromophore⁵⁹ at λ_{max} 253.8 nm (ϵ 215), 256.7 (236) and 263.5 (179) was observed in the ultraviolet spectrum.

Treatment of alcohol (5) with meta-chloroperbenzoic acid in ether gave the 3,4-epoxy-1-phenyl-1-butanols (6). The mass of the parent ion (M^+ 164.0833) in the mass spectrum is consistent with the compound having the molecular formula $C_{10}H_{12}O_2$. The pmr spectrum indicated a multiplet ($W_{\frac{h}{2}}$ 14 Hz) centred at δ 1.88 (C(2)H₂) and the C(3)H and C(4)H₂ appeared as a complex multiplet between δ 2.28 - 3.50. The hydroxy appeared as a broad singlet ($W_{\frac{h}{2}}$ 13 Hz) centred at δ 3.22. The C(1)H and the aromatic protons were multiplets centred at δ 4.80 and δ 7.28 respectively. The infrared spectrum showed absorptions due to hydroxyl, epoxy and aromatic moieties at 3460 cm^{-1} , 840 cm^{-1} and 760 cm^{-1} , and 710 cm^{-1} respectively and the ultraviolet spectrum confirmed the presence of an aromatic chromophore⁵⁹.

Oxidation of the 3,4-epoxy-1-phenyl-1-butanols (6) with chromium trioxide-pyridine complex in anhydrous dichloromethane⁶⁰ gave 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1). The infrared spectrum showed the conjugated carbonyl absorption at 1686 cm^{-1} and the presence of this chromophore was further confirmed by the observation of an intense ultraviolet absorption at $\lambda_{\text{max}}^{\text{EtOH}}$ 243 nm (ϵ 2.44×10^4). The pmr spectrum showed the C(2) protons coupled with each other and with C(3)H. These three protons appeared as a multiplet between δ 3.10 - 3.60. The C(4) proton trans to C(3)H was a doublet of doublets (J 5 Hz, J' 2.5 Hz) centred at δ 2.55. The other C(4) proton cis to C(3)H was more deshielded⁶¹ and appeared as a doublet of doublets

(J 5 Hz, J' 4.0 Hz) centred at δ 2.87. The aromatic protons appeared as two multiplets centred at δ 7.50 (3H's) and δ 7.90 (2H's). The epoxide was relatively unstable and no parent ion could be detected in the mass spectrum. Attempts to purify the epoxide (1) by chromatography on alumina resulted in the isolation of 2-phenylfuran (7)⁶². On standing for 3-4 months at 0°, 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1) rearranged to give a crystalline product, 4-hydroxy-1-phenyl-2-buten-1-one (8) (mp 69 - 71°) which rapidly rearranged to 2-phenylfuran (7) in the presence of a catalytic amount of concentrated hydrochloric acid in methanol. The rearrangement of 3,4-epoxy-1-phenyl-1-butanone (1) to 2-phenylfuran (7) which occurred during attempts to purify the ketone (1) is therefore thought to proceed via 4-hydroxy-1-phenyl-2-buten-1-one (8) as shown in Scheme XVII. A product analogous to alcohol (8),

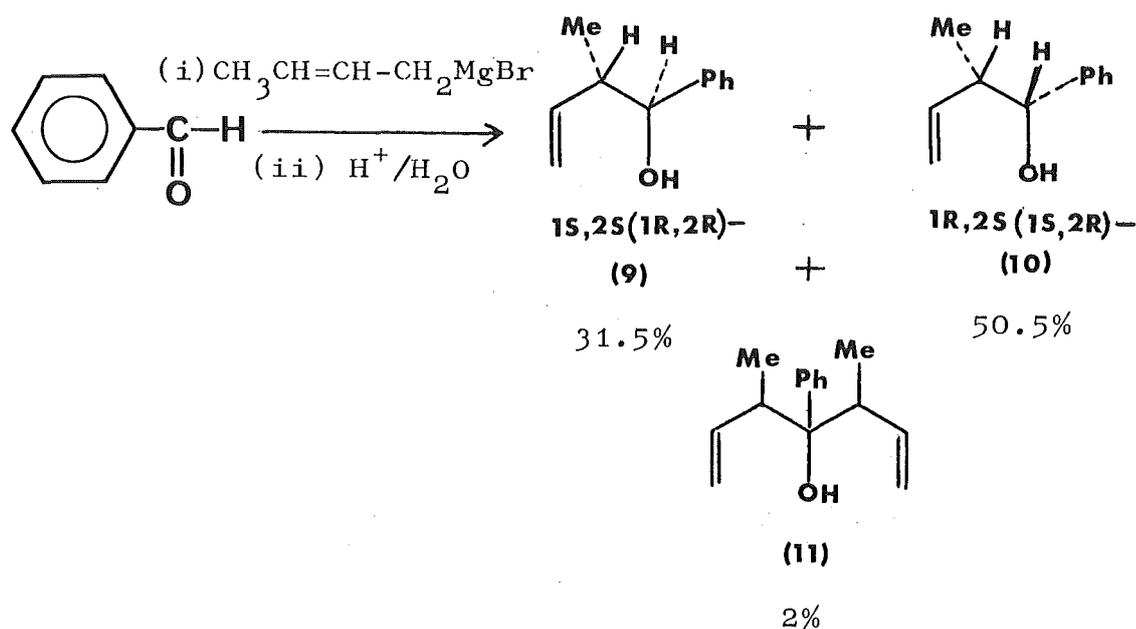


Scheme XVII

namely, Z-1,2-diphenyl-4-hydroxy-2-buten-1-one, has been observed in the pyridine catalysed decomposition⁶³ of 3,4-epoxy-1,2-diphenyl-1-butanone. The pmr spectrum of alcohol (8) showed the C(2) and C(3) olefinic protons as a multiplet centred at $\delta 7.20$. The C(4) methylene protons were centred at $\delta 4.50$ being markedly deshielded by hydroxyl and alkene moieties. Attempts to determine the C(2)H and C(3)H coupling constant by addition of $\text{Eu}(\text{fod})_3$ shift reagent were not successful due to peak broadening. The aromatic protons appeared between $\delta 7.33$ - 8.13 . The solution infrared spectrum of 4-hydroxy-1-phenyl-2-buten-1-one (8) in chloroform indicated, by the intense absorptions at 3475 , 1672 and 1623 cm^{-1} , the presence of hydroxyl, carbonyl and alkene functions respectively. An intense ultraviolet absorption at $\lambda 257.2 \text{ nm}$ ($\epsilon 2.2 \times 10^4$) in ethanol confirmed the presence of a conjugated ketone and the mass spectrum was consistent with the assigned molecular formula.

Reaction of the magnesium Grignard reagent formed from (E)-1-bromo-2-butene with benzaldehyde in ether at 0° gave a mixture of 1S,2S(1R,2R)- and 1R,2S(1S,2R)- 2-methyl-1-phenyl-3-buten-1-ols (9) and (10) and 3,5-dimethyl-4-phenyl-1,6-heptadien-4-ol (11) in 31.5, 50.5 and 2% yields respectively (Scheme XVIII).

The pmr spectrum of 3,5-dimethyl-4-phenyl-1,6-heptadien-4-ol (11) shows the methyls as a doublet centred at $\delta 0.89$ and coupled ($J 7 \text{ Hz}$) with an adjacent methine hydrogen. The C(3)H and C(5)H are each coupled with methyl and the adjacent vinyl proton ($J 8 \text{ Hz}$). The

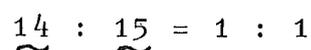
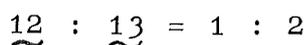
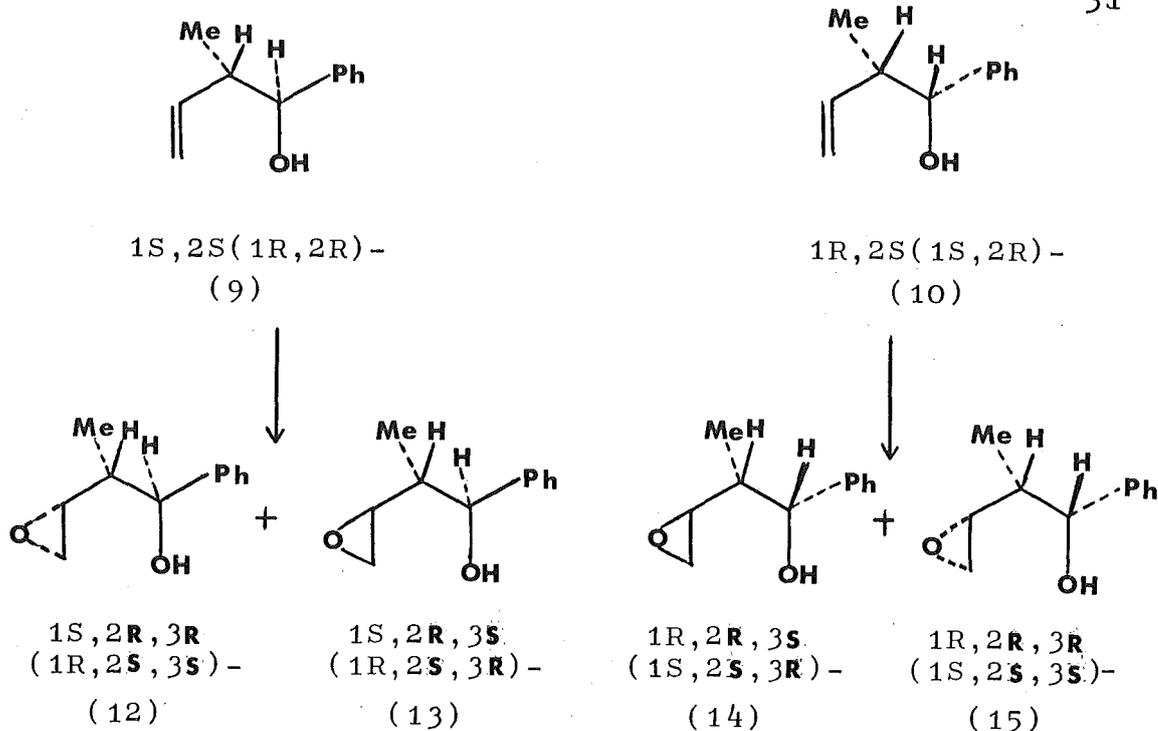


Scheme XVIII

olefinic protons occur as a recognisable ABCX multiplet between δ 4.90 - 6.00 and the five aromatic hydrogens occur as a multiplet centred at δ 7.33. The hydroxyl proton is apparent as a singlet at δ 2.25 which disappears on exchange with D_2O . The hydroxy is also apparent from the infrared spectrum which shows an absorption at 3600 cm^{-1} . The ultraviolet spectrum showed absorption characteristic of a phenyl chromophore.⁵⁹ 3,5-Dimethyl-4-phenyl-1,6-heptadien-4-ol (11) is believed to be formed by disproportionation between the initially produced 2-methyl-1-phenyl-3-buten-1-ols and benzaldehyde to give 2-methyl-1-phenyl-3-buten-1-one which on reaction with excess organo-magnesium Grignard reagent gives 3,5-dimethyl-4-phenyl-1,6-heptadien-4-ol (11).

The two major products, the diastereomeric 2-methyl-1-phenyl-3-buten-1-ols (9) and (10) were separated by repeated chromatography on alumina^{64,65}. The pmr spectrum of the isomers showed the C(2)H and olefinic protons as multiplets centred at δ 2.48 (2.42) and δ 5.00 - 6.15 (4.80 - 6.00) respectively, and the phenyls as multiplets centred at δ 7.30. The C(2) methyl and C(1)H for each isomer had slightly different chemical shifts and the coupling constants between C(1)H and C(2)H were different. The methyl and C(1)H of the major isomer (10) were downfield, δ 0.97 and δ 4.50 compared with the minor isomer (9), δ 0.83 and δ 4.37 respectively, and the C(1)H - C(2)H coupling constant of 6 Hz for the major isomer (10) was slightly smaller than for the minor isomer (9) (J 8 Hz). An assignment of the relative configuration at C(1) and C(2) based on these small differences in the pmr spectra or on the relative yield of the isomers formed was considered inadequate and the configuration was therefore determined by rigorous methods.

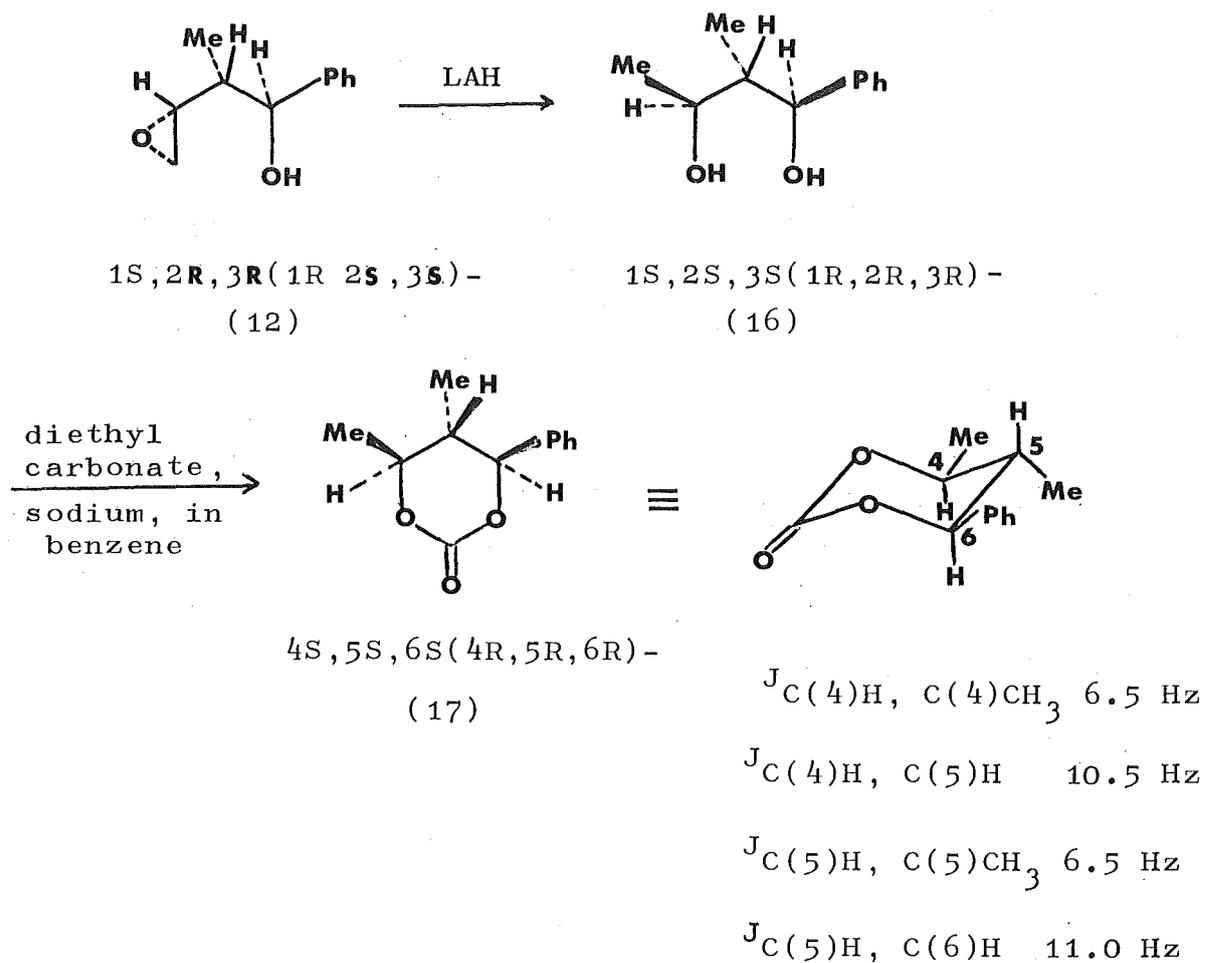
Epoxidation of a mixture of the 2-methyl-1-phenyl-3-buten-1-ols (9) and (10) with meta-chloroperbenzoic acid in ether gave the four enantiomeric pairs of 3,4-epoxy-2-methyl-1-phenyl-1-butanols (Scheme XIX). A pure sample of olefin (10) on epoxidation gave two enantiomeric pairs of epoxides in a 1 : 1 ratio and epoxidation of olefin (9) similarly gave two pairs of epoxides in the ratio 1 : 2. The later epoxides were different from those obtained from olefin (10). From the reaction mixture of epoxides obtained by epoxidation of a mixture of olefins (9) and (10), only small



Scheme XIX

quantities of the most and least polar 3,4-epoxy-2-methyl-1-phenyl-1-butanols (12) and (15) could be separated.

In order to determine the stereochemistry of these compounds, it was decided to attempt to lock a derivative which had been stereospecifically formed from one or more of the compounds into a rigid six-membered ring system. It was hoped that a measure of the pmr coupling constants between neighbouring protons would allow an assignment of the relative configurations to be made. Reaction of the most polar 3,4-epoxy-2-methyl-1-phenyl-1-butanol (12) with lithium aluminium hydride in anhydrous ether gave a 2-methyl-1-phenyl-1,3-butanediol (16) in high yield (Scheme XX). Repeated attempts were made to react the 1,3-diol (16) with formaldehyde and acetone to produce a cyclic



Scheme XX

compound⁶⁶ which would allow the relative stereochemistry at C(1), C(2) and C(3) of the diol to be determined.

These reactions were however not successful. Reaction of the 1,3-diol (16) with diethyl carbonate afforded⁶⁷ a liquid product that had a pleasant smell characteristic of a cyclic carbonate or 1,3-dioxacyclohexan-2-one.

Infrared studies revealed strong absorptions at 1755 cm^{-1} (carbonyl), 1252 and 1198 cm^{-1} (carbonate) and 769 and 709 cm^{-1} (aromatic). The mass of the parent ion (M^+ 206.0946) was consistent with a molecular formula of $C_{12}H_{14}O_3$. The parent ion extrudes CO_2 and

an intense peak of mass 162 ($M^+ - CO_2$) was observed. The required information, namely the stereochemistry at C(4), C(5) and C(6) was provided from a detailed study of the pmr spectrum of the cyclic carbonate (17) and is shown in Table IV. The coupling constants $J_{C(5)H,C(6)H}$ and $J_{C(5)H,C(4)H}$ have values of 11.0 Hz and 10.5 Hz respectively. The large values of these couplings show that these protons are axial and trans to each other. These data is consistent with structure

Table IV Pmr data of 4S,5S,6S(4R,5R,6R)-4,5-dimethyl-6-phenyl-1,3-dioxacyclohexan-2-one (17)
 (Values in parenthesis are for 4S,5S,6R(4R,5R,6S)-4,5-dimethyl-6-phenyl-1,3-dioxacyclohexan-2-one (19))

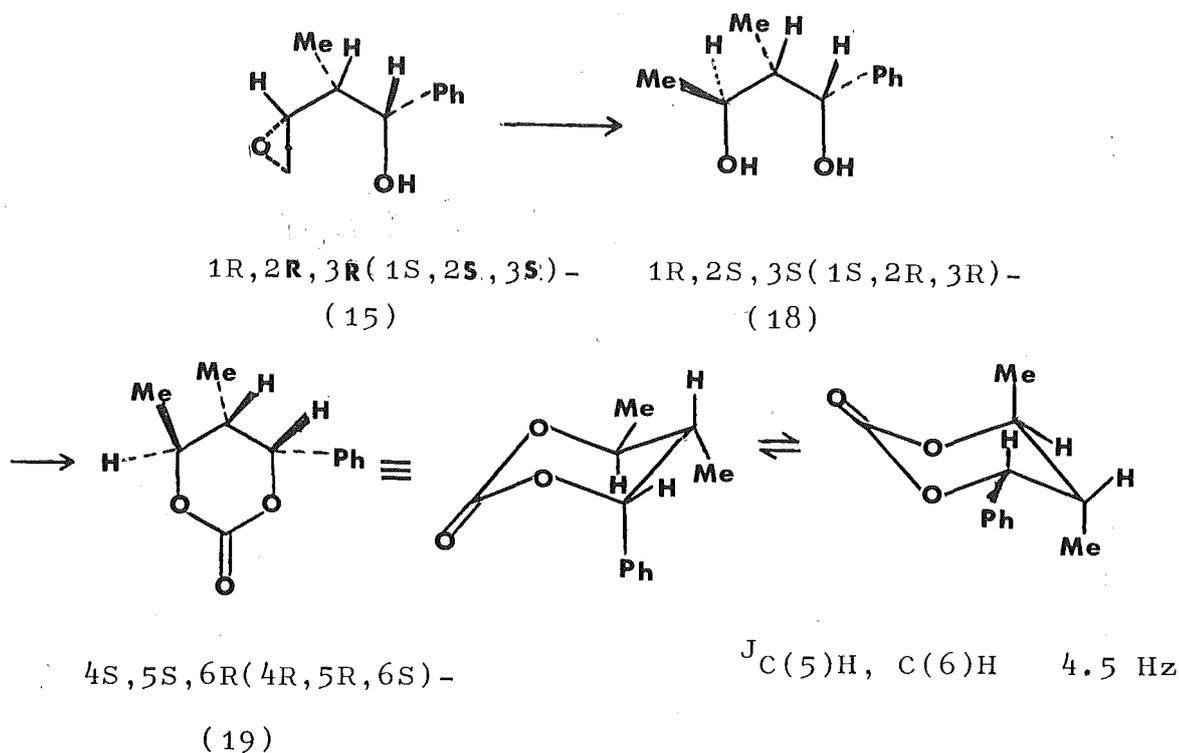
	C(4)H	C(4)Me	C(5)H	C(5)Me	C(6)H	C(6)Ph
Chemical shift in ppm ^a	4.37 (4.42)	1.45 (1.45)	1.93 (2.23)	0.80 (0.84)	4.95 (5.57)	7.40 (7.38)
pattern	d of q (d of q)	d (d)	m, $\frac{W}{2}$ 40 Hz (m, $\frac{W}{2}$ 40 Hz)	d (d)	d (d)	m, $\frac{W}{2}$ 3 Hz (m, $\frac{W}{2}$ 3 Hz)
J values in Hz	10.5, 6.5 b (?, 7.0)	6.5 (7.0)	10.5,11.0, 6.5 b (?, 7.0 4.5)	6.5 (7.0)	11.0 (4.5)	

a, Determined at 60 MHz for a 10% solution (W/V) in $CDCl_3$ with $CHCl_3$ and $(CH_3)_4Si$ as internal standards.

b, J values cannot be determined accurately.

(17) where the C(6) phenyl, C(5) and C(4) methyls are all equatorial. The cyclic carbonate can therefore be assigned as 4*S*,5*S*,6*S*(4*R*,5*R*,6*R*)-4,5-dimethyl-6-phenyl-1,3-dioxacyclohexan-2-one (17). The stereochemistry at C(4), C(5) and C(6) for the cyclic carbonate (17) defines the structural formula for the starting diol as 1*S*,2*S*,3*S*(1*R*,2*R*,3*R*)-2-methyl-1-phenyl-1,3-butanediol (16). This in turn allows the assignment of stereochemistry to its precursor 1*S*,2*R*,3*R*-(1*R*,2*S*,3*S*)-3,4-epoxy-2-methyl-1-phenyl-1-butanol (12) (Scheme XX).

A similar reaction sequence for the least polar epoxybutanol (15) (Scheme XXI) gave the 1,3-dioxacyclohexan-2-one (19) and the pmr data for this compound



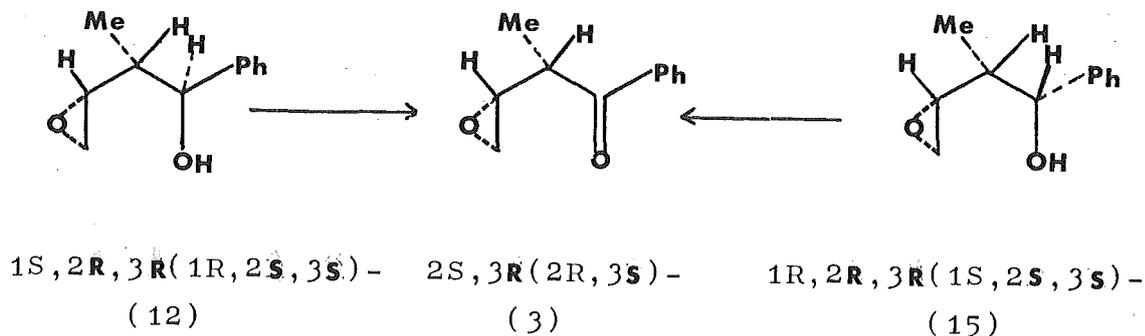
Scheme XXI

is shown in parenthesis in Table IV. The important difference between the cyclic dioxanones (17) and (19) is the magnitude of coupling constant between C(6)H and C(5)H which is 11.0 Hz for 17 and 4.5 Hz for 19. This difference reflects the difference in stereochemistry at C(6) and the J value of 4.5 Hz in compound (19) indicates either that the C(6)H is cis to the C(5)H or that the C(5) methyl and C(6) phenyl are both axial. This latter situation can be excluded on energetic grounds and therefore compound (19) can be assigned as 4S,5S,6R(4R,5R,6S)-4,5-dimethyl-6-phenyl-1,3-dioxacyclohexan-2-one. The precursors to 19 can therefore be assigned as 1R,2S,3S(1S,2R,3R)-2-methyl-1-phenyl-1,3-butanediol (18) and 1R,2R,3R(1S,2S,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanol (15). The structural assignment of 1S,2R,3R(1R,2S,3S)- and 1R,2R,3R(1S,2S,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanols (12) and (15) was confirmed by the observation that separate oxidation of these compounds with chromium trioxide-pyridine complex in dichloromethane gave a single epoxyketone. As the 3,4-epoxy-2-methyl-1-phenyl-1-butanols (12) and (13) were derived from 2-methyl-1-phenyl-3-buten-1-ol (9), they are therefore diastereomers. Such a relationship permits the assignment of 13 as 1S,2R,3S(1R,2S,3R)-3,4-epoxy-2-methyl-1-phenyl-1-butanol (Scheme XIX).

Similar reasoning allows the stereochemistry of 14, the diastereomer of 1R,2R,3R(1S,2S,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanol (15) to be assigned as

1R,2R,3S(1S,2S,3R)-3,4-epoxy-2-methyl-1-phenyl-1-butanol (14).

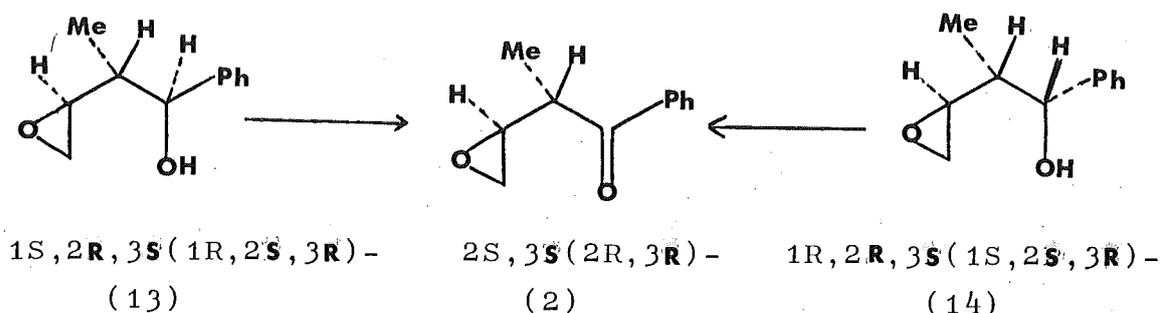
The relative stereochemistry at C(1) and C(2) in butenol (9), the precursor of epoxyalcohols (12) and (13) can therefore be assigned and the compound is therefore 1S,2S(1R,2R)-2-methyl-1-phenyl-3-buten-1-ol. The butenol (10) is therefore 1R,2S(1S,2R)-2-methyl-1-phenyl-3-buten-1-ol. Since oxidation of the 1S,2R,3R(1R,2S,3S)- and 1R,2R,3R(1S,2S,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanols (12) and (15) gave epoxyketone (3), the structure of the epoxyketone can be assigned as 2S,3R(2R,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanone (3) (Scheme XXII). The pmr spectrum of epoxyketone (3)



Scheme XXII

has a doublet (J 7 Hz) centred at $\delta 1.26$ ($C(2)CH_3$), multiplets centred at $\delta 3.25$ ($C(2)H$ and $C(3)H$) and $\delta 2.72$ ($C(4)H_2$) and two characteristic aromatic clusters at $\delta 7.48$ ($3H's$) and $\delta 7.95$ ($2H's$). Except for the difference in chemical shift of $C(2)CH_3$ ($\delta 1.38$ cf. $\delta 1.26$ in 3) the isomeric epoxyketone 2S,3S(2R,3R)-3,4-epoxy-2-methyl-1-phenyl-1-butanone (2) has an almost identical pmr spectrum. The spectrum of this compound was obtained by

oxidation of mixtures of epoxyalcohols containing 1S,2R,3S(1R,2S,3R)- and 1R,2R,3S(1S,2S,3R)- 3,4-epoxy-2-methyl-1-phenyl-1-butanols (13) and (14) (Scheme XXIII). The infrared spectrum of a mixture

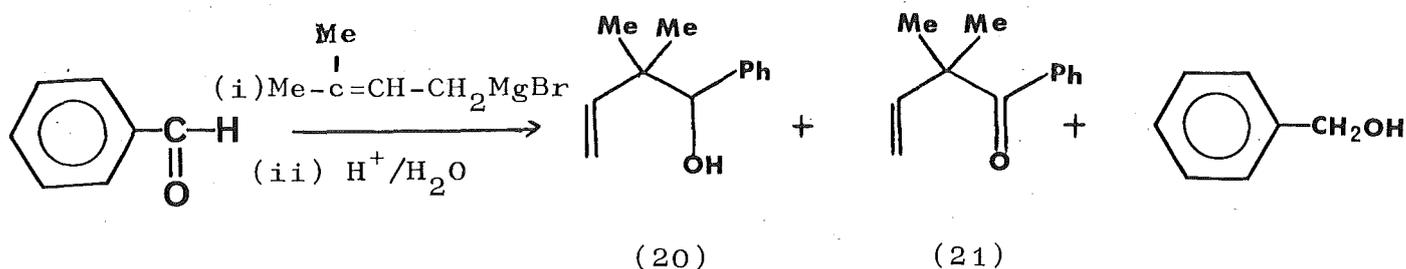


Scheme XXIII

of 3 and 2 confirmed the presence of the conjugated ketone chromophore (1685 cm^{-1}) and the ultraviolet spectrum ($\lambda_{\text{max}}^{\text{EtOH}}$ 243.0 nm, ϵ_{max} 1.23×10^4) (Table V) confirmed the presence of this chromophore. The mass spectrum showed a parent ion of mass 176.0843 consistent with a molecular formula $C_{11}H_{12}O_2$.

For the preparation of 3S(3R)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4), 1-bromo-3-methyl-2-butene was required and was prepared⁶⁸ from 2-methyl-1,3-butadiene. Reaction of the organo-magnesium Grignard reagent prepared from 1-bromo-3-methyl-2-butene with benzaldehyde gave a mixture of 2,2-dimethyl-1-phenyl-3-buten-1-ol (20), 2,2-dimethyl-1-phenyl-3-buten-1-one (21) and benzyl alcohol in modest yields

(12, 11 and 15% respectively) (Scheme XXIV). 2,2-Dimethyl-1-phenyl-3-buten-1-ol (20) was identified⁶⁴

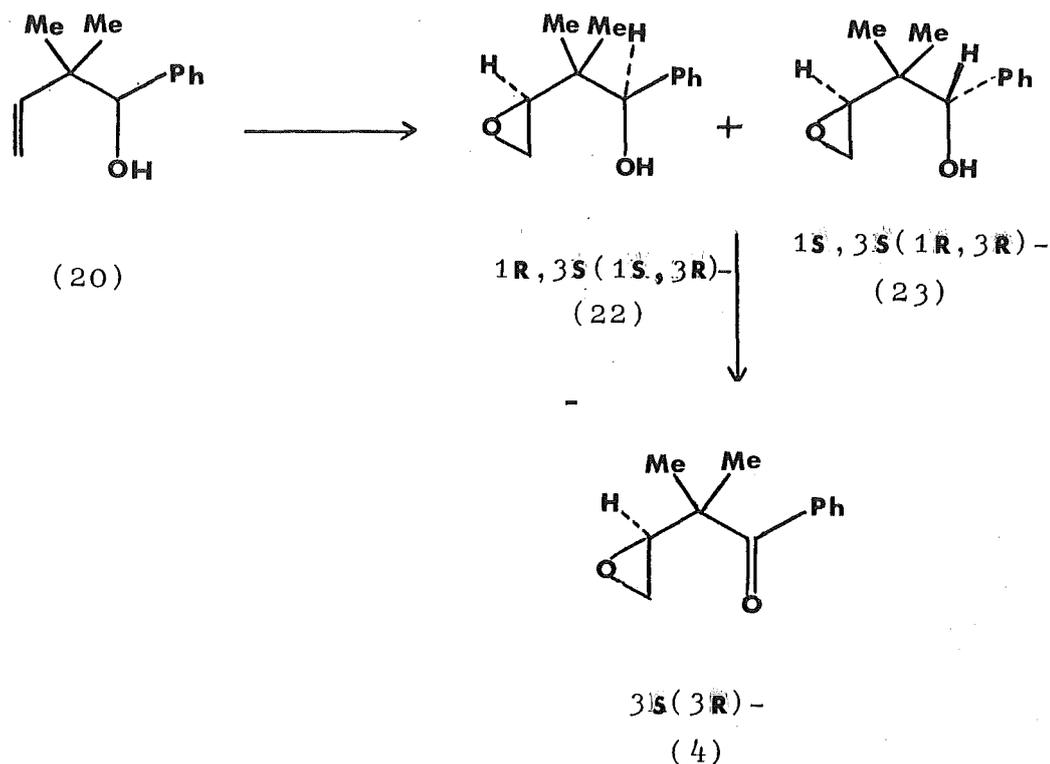


Scheme XXIV

from the infrared and pmr spectra which showed the C(1)H as a doublet (J 3 Hz) centred at δ 4.37 coupled with OH. On exchange of the latter proton by shaking with D_2O , the C(1)H signal collapsed to a singlet. The three olefinic protons appeared as a complex multiplet between δ 4.83 - 6.20. The C(2) methyls appeared as two singlets at δ 1.00 and 0.95 while the aromatic protons were a multiplet centred at δ 7.27. The assignment of the structure to 2,2-dimethyl-1-phenyl-3-buten-1-one (21) follows from the spectral data obtained. This compound has recently been reported⁶⁹ but only limited spectral data was published. The mass spectrum of 2,2-dimethyl-1-phenyl-3-buten-1-one (21) gave a parent ion of mass 174.1048, consistent with the molecular formula $\text{C}_{12}\text{H}_{14}\text{O}$. The infrared spectrum showed sharp absorptions at 1681, 975 and 923, and 708 cm^{-1} corresponding to carbonyl, alkene and aromatic functions respectively. The ultraviolet spectrum ($\lambda_{\text{max}}^{\text{EtOH}}$ 243.7 nm (ϵ 9.2×10^3)) confirmed

the presence of a conjugated ketone chromophore. The pmr spectrum in deuteriochloroform showed the C(3)H as a doublet of doublets centred at δ 6.20, coupled (J 10 Hz, J' 18 Hz) to the C(4)H₂ which appeared as a complex multiplet centred at δ 5.20. The formation of 2,2-dimethyl-1-phenyl-3-buten-1-one (21) and benzyl alcohol in this reaction are believed to result from disproportionation of benzaldehyde and 2,2-dimethyl-1-phenyl-3-buten-1-ol (20).

Epoxidation of 2,2-dimethyl-1-phenyl-3-buten-1-ol (20) with meta-chloroperbenzoic acid gave the 3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanols (22) and (23) in high yield. The structures of the products were consistent with the mass of the parent ion in the mass spectrum. The infrared spectrum showed absorptions due to hydroxyl, epoxy and aromatic functions at ν_{\max} 3455, 910 and 865, and 733 and 710 cm⁻¹ respectively. In the pmr spectrum the methyls of one enantiomeric pair of diastereoisomers occur at δ 0.80. The methyls of the other diastereoisomers are centred at δ 0.83 and δ 0.75. The C(1)H of each isomer is coupled with the hydroxyl proton and appear as doublets centred at δ 4.48 and 4.55 respectively. The epoxy protons of these compounds are observed as multiplets centred at δ 2.57 (C(4)H₂) and δ 2.88 (C(3)H). Oxidation of the 3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanols (22) and (23) with excess of chromium trioxide-pyridine complex (1 : 6 ratio) gave a quantitative yield of 3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) (Scheme XXV). The infrared spectrum



Scheme XXV

showed an intense peak at 1681 cm^{-1} , indicative of a conjugated carbonyl chromophore. The ultraviolet spectrum with an intense absorption at 244.2 nm ($\epsilon 0.80 \times 10^4$) confirmed the presence of this chromophore. The mass of the parent ion in the mass spectrum was consistent with the required molecular formula. In the pmr spectrum, the C(2) methyls appeared as a singlet at $\delta 1.28$. The C(3)H centred at $\delta 3.20$ was a doublet of doublets ($J\ 3\text{ Hz}$, $J'\ 4.5\text{ Hz}$) while the C(4)H₂ was a multiplet centred at $\delta 2.80$. The methyls of 3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) are deshielded ($\delta 1.28$) by the carbonyl compared with the methyls of the 3,4-epoxy-2,2-dimethyl-1-phenyl-1-

butanols (δ 0.80 and (δ 0.83, δ 0.75)).

The ultraviolet spectra of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1), a mixture of 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3) and 3S(3R)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) (Table V) show strong absorptions due to the presence of the α , β -unsaturated ketone chromophore. The intensity of shorter wavelength absorption decreases with increasing substitution at C(2) and compares favourably with those values reported for 3,4-epoxy-1,4-diphenyl-1-butanone⁴⁹ and 3,4-epoxy-1,2-diphenyl -1-butanone⁶³. The higher wavelength absorptions have not been reported for these latter ketones.

Table V

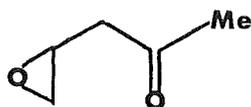
Ultraviolet absorption data (in ethanol)

Compound	λ_{\max} (nm)	$\epsilon_{\max} \times 10^4$	λ_{\max} (nm)	$\epsilon_{\max} \times 10^3$	λ_{\max} (nm)	ϵ_{\max}
3,4-epoxy-1-phenyl-1-butanone	243.0	2.44	279.0	1.08	328.0	57
3,4-epoxy-2-methyl-1-phenyl-1-butanones	243.0	1.23	279.0	1.04	327.0	77
3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone	244.2	0.80	278.5	0.76	323.0	138
3,4-epoxy-1,4-diphenyl-1-butanone ^a	243	1.4	277	1.00		
3,4-epoxy-1,2-diphenyl-1-butanone ^b	247	1.3				

a, data taken from reference 49

b, data taken from reference 63

An attempt was made to synthesise 4,5-epoxy-2-pentanone (24) since it was thought that this compound might react from an excited singlet state. Two alternative synthetic routes were explored. The first in-

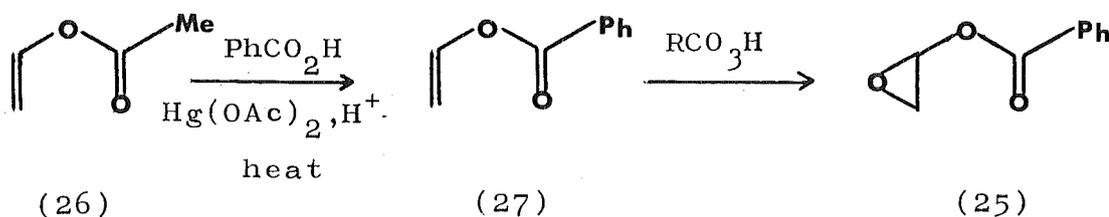


(24)

involved epoxidation of 4-penten-2-ol with meta-chloroperbenzoic acid in ether to give 4,5-epoxy-2-pentanol which on oxidation would be expected to give 4,5-epoxy-2-pentanone (24). Attempts to effect this latter oxidation with chromium trioxide-pyridine complex in dichloromethane led only to decomposition of the epoxyalcohol. Attempts at oxidation with active manganese dioxide in dichloromethane, and ruthenium tetroxide in carbon tetrachloride were unsuccessful. An alternative scheme involving the preparation of 4-penten-2-one from the reaction of organo-magnesium Grignard of 1-bromo-2-propene with acetic anhydride and epoxidation of the unsaturated ketone with meta-chloroperbenzoic acid in ether failed at the epoxidation step.

The synthetic route (Scheme XXVI) to oxiranyl

benzoate (25) involved ester-exchange⁷⁰ on ethenyl acetate (26) to give ethenyl benzoate (27) along with high boiling diester by-products. The aromatic protons of ethenyl benzoate (27) absorb at δ 7.33 - 8.20 in its pmr spectrum. The C(2)H trans to the benzoate group appears as a doublet of doublets (J 7.0 Hz and J' 1.5 Hz) centred at δ 4.65 while the other terminal olefinic proton cis to the benzoate group appears as a doublet



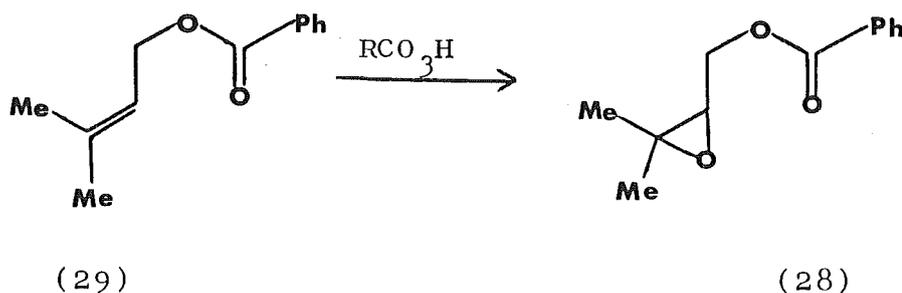
Scheme XXVI

of doublets centred at δ 5.03, but with coupling constants of J 14.0 Hz and J' 1.5 Hz. The C(1) proton is deshielded and appears in the aromatic region of the spectrum. The infrared spectrum shows the presence of ester (1737, 1247 cm⁻¹) and monosubstituted aromatic (715, 702 cm⁻¹) functions. The parent ion in the mass spectrum has a mass of 148.0522 consistent with the molecular formula C₉H₈O₂. Other prominent peaks have masses of 105 and 77 corresponding to (C₆H₅CO)⁺ and (C₆H₅)⁺ fragments respectively. Epoxidation of ethenyl benzoate (27)

with meta-chloroperbenzoic acid in dichloromethane gave oxiranyl benzoate (25). In the pmr spectrum of 25, the C(1)H appeared as a doublet of doublets (J 2.5 Hz, J' 1.0 Hz) centred at δ 5.80 while the C(2)H₂'s were a multiplet ($W\frac{h}{2}$ 9 Hz) centred at δ 2.97. The chemical shift of the aromatic protons does not change significantly on epoxidation (δ 7.40 - 8.01 cf. δ 7.33 - 8.20 in 27).

The mass spectrum of oxiranyl benzoate (25) has a parent ion at 164.0470 (C₉H₈O₃) and peaks for the expected benzoyl and phenyl fragments. Oxiranyl benzoate (25) is not unexpectedly unstable and decomposes on standing to give a mixture from which benzoic acid could be isolated.

2,3-Epoxy-3-methyl-1-butanol benzoate (28) was synthesised from 3-methyl-2-buten-1-ol benzoate (29) which was prepared⁷¹ from the reaction of sodium benzoate with 1-bromo-3-methyl-2-butene. The alkenyl benzoate (29) was identical to a sample obtained as a product of photolysis of 3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4). Treatment of 3-methyl-2-buten-1-ol benzoate (29) with meta-chloroperbenzoic acid in ether under reflux for 2½ hours gave 2,3-epoxy-3-methyl-1-butanol benzoate (28) (Scheme XXVII). The methyls appeared as a singlet centred at δ 1.38.

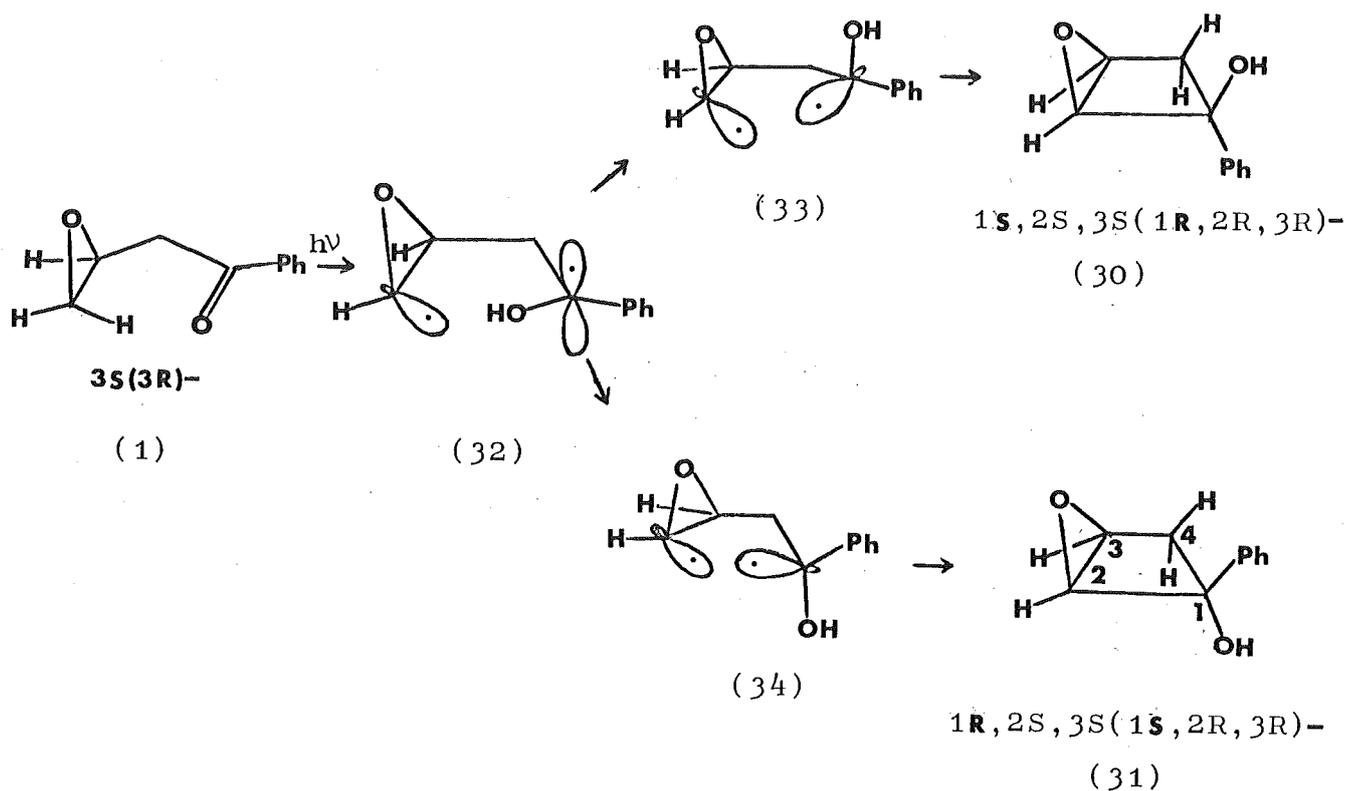


Scheme XXVII

in the pmr spectrum and the C(2)H was a doublet of doublets centred at $\delta 3.13$. The C(1)H₂ was a A,B quartet ($\delta_A 4.34$, $\delta_B 4.60$) and each proton was further coupled ($J 6.5$ Hz, $J' 4.5$ Hz respectively) with C(2)H. The aromatic protons absorbed between $\delta 7.40 - 8.23$.

Photolysis of β,γ -epoxycarbonyl compounds

A solution of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1) in anhydrous, degassed benzene, under a nitrogen atmosphere, was irradiated in a pyrex container with 3000 Å lamps⁷². The reaction vessel had been washed with base to prevent acid catalysed reaction of the starting epoxide. The photolysis reaction was complete in 19 hours and gave a mixture of 1S,2S,3S (1R,2R,3R)-2,3-epoxy-1-phenyl-1-cyclobutanol (30) (47%) and 1R,2S,3S(1S,2R,3R)-2,3-epoxy-1-phenyl-1-cyclobutanol (31) (28%) (Scheme XXVIII). The pmr spectrum of epoxy-cyclobutanol (31) showed four apparent singlets centred at $\delta 2.02$ (OH), $\delta 2.27$ (C(4)H₂), $\delta 3.90$ (C(2)H and C(3)H) and $\delta 7.30$ (C₆H₅). This contrasts with the more complicated spectrum of the isomeric epoxycyclobutanol (30) which showed a singlet at $\delta 2.92$ (OH) and epoxy and aromatic protons as multiplets centred at $\delta 3.97$ and $\delta 7.33$ respectively. The two methylene protons



Scheme XXVIII

appeared as an A,B quartet with the upfield proton further coupled (J 2.5 Hz) (Figure III in Experimental). On addition of a small quantity of $\text{Eu}(\text{fod})_3$ to solutions of epoxycyclobutanols (30) and (31) in deuteriochloroform, the spectra became remarkably similar as the chemical shifts of the methylene protons and epoxide protons of epoxide (31) became different.

The relative stereochemistry of epoxycyclobutanols (30) and (31) were assigned from pmr studies on addition of $\text{Eu}(\text{fod})_3$ (Table VI). In the pmr spectrum of epoxycyclobutanol (30), the C(2)H and the C(3)H appeared as a multiplet centred at δ 3.97. On addition of $\text{Eu}(\text{fod})_3$, the C(2)H emerged as a doublet of

Table VI. Pmr data^a for epoxycyclobutanols (30) and (31)

Compound	Group	Shift (ppm) ^a	Coupling Constants (Hz) ^a
(30)	C(1)-phenyl	7.33 $W\frac{h}{2}$ 22 Hz (8.40 $W\frac{h}{2}$ 10), (7.50 $W\frac{h}{2}$ 10)	
	C(2)-H	3.97	(6.12) $J_{2,3}$ 2 $J_{2,4a}$ 2.5
	C(3)-H	3.97	(5.72) $J_{2,3}$ 2
	OH	2.92	(7.70)
	C(4)-H _b	2.50	(3.97) $J_{4b,4a}$ 12.5
	C(4)-H _a	2.02	(4.28) $J_{4a,4b}$ 12.5 $J_{4a,2}$ 2.5
(31)	C(1)-phenyl	7.30 $W\frac{h}{2}$ 5 Hz (8.30 $W\frac{h}{2}$ 12) (7.48 $W\frac{h}{2}$ 8)	
	C(3)-H	3.90	(5.15) $s(J_{3,2})$ 2)
	C(2)-H	3.90	(5.52) $s(J_{2,3})$ 2) $(J_{2,4b})$ 2)
	C(4)-H _a	2.27	(3.11) $s(J_{4a,4b})$ 12)
	C(4)-H _b	2.27	(3.40) $s(J_{4b,4a})$ 12) $(J_{4b,2})$ 2)
	OH	2.02 $W\frac{h}{2}$ 6 Hz (4.95)	

^a Determined at 60 MHz for a 10% solution (W/V) in $CDCl_3$ with $CHCl_3$ and Me_4Si as internal standards. Figures in parenthesis were obtained after addition of $Eu(fod)_3$.

doublets (J 2 Hz, J' 2 Hz) which was deshielded relative to the C(3)H. The C(4)H_a syn to epoxide and hydroxy was upfield of C(4)H_b which must be in the deshielding region of the phenyl group. On addition of shift reagent, C(4)H_a moved rapidly downfield (C(4)H_a : C(4)H_b compared with C(3)H, 1.29 : 0.84). Long range coupling between C(2)H and C(4)H_a was established. For epoxycyclobutanol (31), C(2)H and C(4)H_b both syn to the hydroxy, were deshielded (1.30 and 0.91 respectively) by the addition of Eu(fod)₃ relative to C(3)H. The C(4)H_a moved downfield, but to a lesser extent in compound (31) than in (30) where it is syn to both oxygen functions. The aromatic protons of 31 are more deshielded on addition of Eu(fod)₃ than the aromatic protons of 30 (0.34, 0.06, cf. 0.22, 0.04 shifts relative to respective OH), consistent with their proximity to both the epoxide oxygen and hydroxy in the former compound.

The configuration of the isomers (30) and (31) was further established by the concentration dependence of the chemical shifts of the hydroxyl protons and their extrapolated values to infinite dilution (ca. δ 2.7 ppm for 30 and ca. δ 1.7 ppm for 31) (Figure IV in Experimental). For a compound exhibiting strong intramolecular hydrogen bonding only a small change in the chemical shift of the hydroxyl proton would be expected with change in concentration. The observation that the chemical shift of the hydroxyl proton in 30 is more deshielded (δ 2.92 cf. δ 2.02 for 31) and has less

dependence on concentration ($\Delta\delta$ ppm) than the corresponding proton in 31 is consistent with the assigned structures of 30 as 1S,2S,3S(1R,2R,3R)-2,3-epoxy-1-phenyl-1-cyclobutanol and 31 as 1R,2S,3S(1S,2R,3R)-2,3-epoxy-1-phenyl-1-cyclobutanol. Similar concentration dependence of the chemical shift of the hydroxyl proton in 2-fluoroethanol has led Griffith⁷³ to conclude that hydrogen bonding is not an important factor in favouring the gauche conformation of 2-fluoroethanol. The infrared solution spectra of the epoxycyclobutanols showed absorptions due to the hydroxy (30, $\nu_{\max}^{\text{CCl}_4}$ 3600 and 3530 cm^{-1} , 31 $\nu_{\max}^{\text{CCl}_4}$, 3620 and 3475 cm^{-1}) and epoxy functions. The absorption due to hydrogen bonded hydroxy (30 3530 cm^{-1} , 31 3475 cm^{-1}), when highly diluted, disappeared from both compounds.

Norrish Type II abstraction of the proximate C(4)H by the excited carbonyl (probably T¹) of 3,4-epoxy-1-phenyl-1-butanone (1) will result in the formation of 1,4-biradical (32) with the radical orbitals orthogonal (Scheme XXVIII). This biradical could either undergo fragmentation to give acetophenone and oxirene derived product or cyclise to cyclobutanol derivatives. Both of these processes were observed in the photolysis⁴⁹ of 3S,4S(3R,4R)-3,4-epoxy-1,4-diphenyl-1-butanone. However, in the photolysis of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1), a fragmentation product (acetophenone) could at best account for only 2% of the reaction. Cyclisation of the biradical to give the isomeric 1S,2S,3S(1R,2R,3R)- and 1R,2S,3S(1S,2R,3R)-

2,3-epoxy-1-phenyl-1-cyclobutanols (30) and (31) in the ratio of 1.67 : 1 respectively was the dominant reaction process. The conformational preference towards the formation of 30 can be understood with reference to conformations (33) and (34) of the biradicals (Scheme XXVIII). The product ratio indicates conformer (33), where the phenyl is anti to the epoxide oxygen, is favoured over conformer (34). The steric interaction between the epoxide oxygen, phenyl or hydroxy will however be small until the 1,4-bond is well developed.

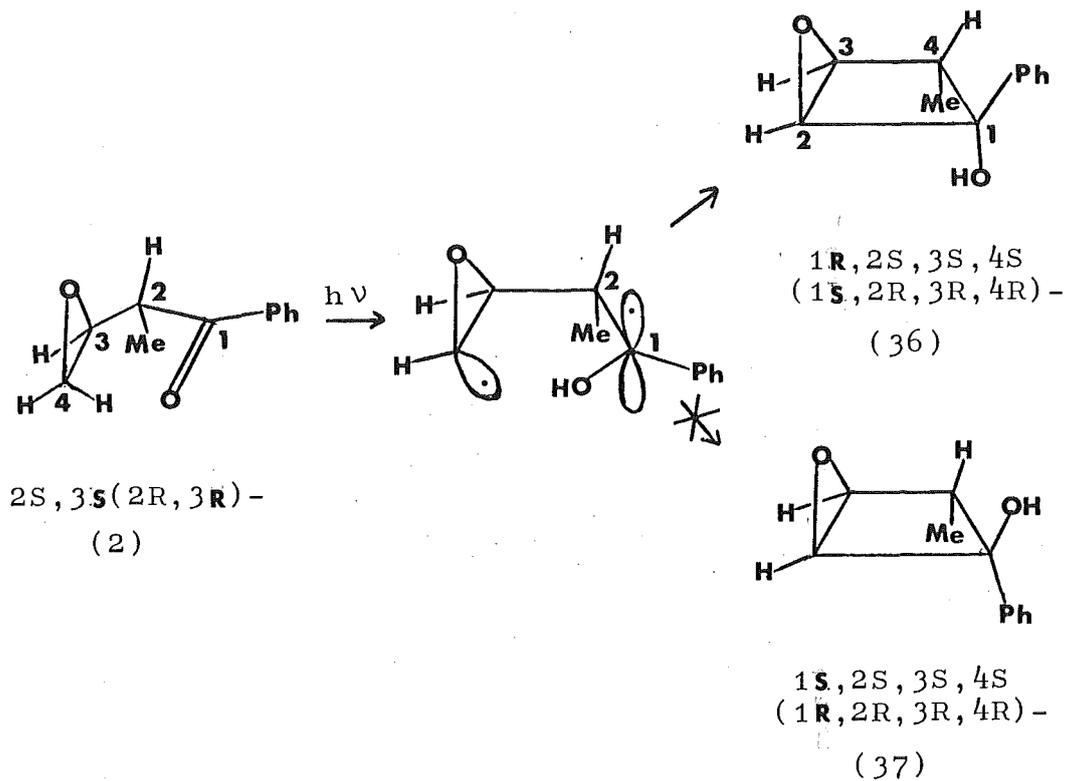
Because of the difficulty in obtaining separate samples of 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3), photolysis experiments were carried out on mixtures from which it was possible by extrapolation to determine the product(s) from each epoxide. In a typical experiment, a mixture of 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3), (0.006M, 2 : 3 ; 2 : 1) in anhydrous benzene was photolysed for 18 hours under the same conditions as those employed in the photolysis of 3,4-epoxy-1-phenyl-1-butanone (1). The reaction gave 1R,2R,3R,4S(1S,2S,3S,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (35) mp 84-5° and 1R,2S,3S,4S(1S,2R,3R,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (36) in 7% and 37% yield respectively and starting mixture (22%) rich in 2S,3R(2R,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanone (3). When the recovered starting material rich in isomer (3) was

subjected to the photolysis for a further 17 hours, only the crystalline 1R,2R,3R,4S(1S,2S,3S,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (35) (42%) was isolated. Photoproduct (35) therefore arises from epoxide (3). Product (36) could not be detected by tlc or pmr and therefore must be formed from ketone (2).

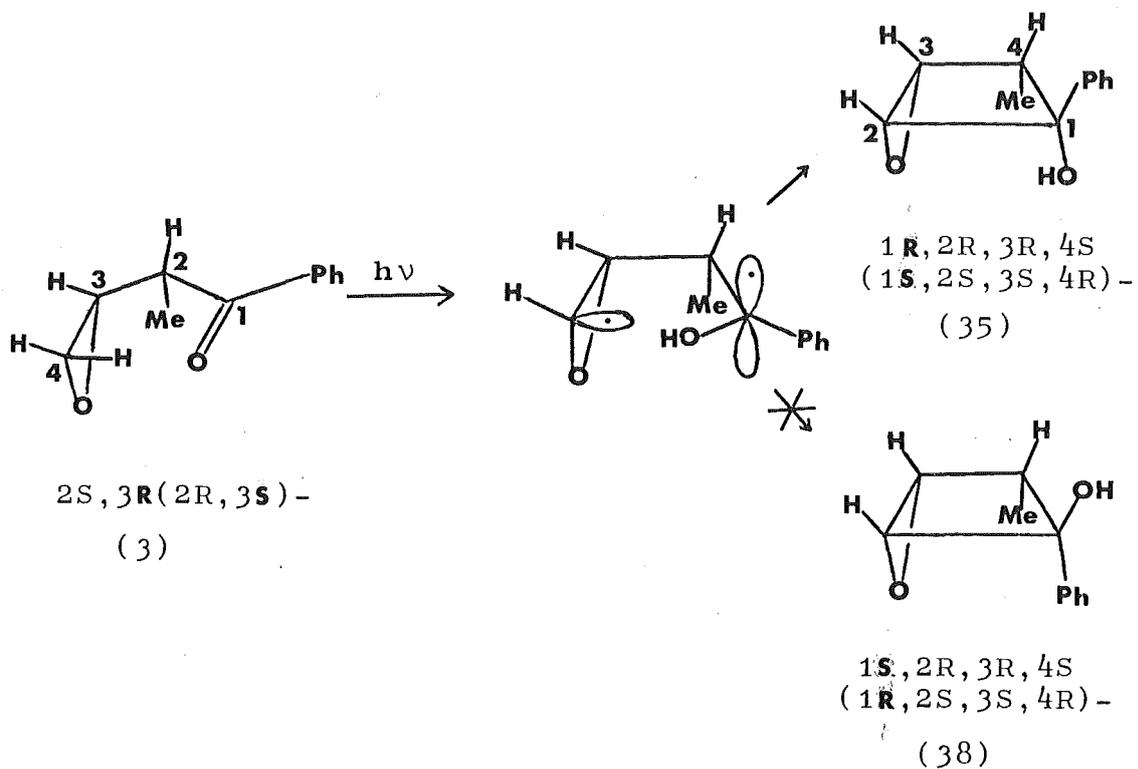
Photoproducts 1R,2R,3R,4S(1S,2S,3S,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (35) (mp 84 - 5°) and 1R,2S,3S,4S(1S,2R,3R,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (36) have similar spectral characteristics. The pmr spectra of these isomers are shown in Figure V in the Experimental. For each isomer a small coupling is observed between C(2)H and C(3)H. For isomer (36) an additional coupling is observed between C(2)H and C(4)H. The infrared spectra show the presence of hydroxy (ν_{\max} 35, 3580 cm^{-1} ; 36, 3594 - 3454 cm^{-1}) and the ultraviolet spectra show absorption due to the phenyl groups. The configuration of the epoxycyclobutanols (35) and (36) at C(2), C(3) and C(4) is defined by the configuration of the starting epoxides (3) and (2) respectively. The effect on the pmr spectra of the addition of $\text{Eu}(\text{fod})_3$ is shown in Figures VI and VII. The configuration at C(1) for both cyclobutanol isomers was determined from pmr dilution studies. The chemical shifts of the hydroxyl protons were measured in solutions of varying concentration and the results extrapolated to give values for the

chemical shifts at infinite dilution. For the cyclobutanol (36) formed from epoxide (2) the chemical shift of the hydroxyl proton was concentration dependent and at infinite dilution a value of $\delta 1.9$ was determined. This compares with a value of $\delta 2.8$ determined for epoxycyclobutanol (35). The change in chemical shift with concentration for this proton was less marked than for the corresponding proton in 36. These values can be compared with those obtained for the epoxycyclobutanols (30) and (31). For isomer (30) where the hydroxyl and epoxide moieties are syn a value for the chemical shift of hydroxyl proton at infinite dilution of $\delta 2.7$ was determined and for the anti-isomer (31) a value of $\delta 1.7$ was obtained. For the isomers where intramolecular hydrogen bonding is possible (i.e. 35 and 30) the chemical shift is less concentration dependent and the proton more deshielded than for isomers (36) and (31) where intramolecular hydrogen bonding is not possible.

Norrish Type II γ -hydrogen abstraction for 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3) would give the orthogonal 1,4-biradicals shown in Schemes XXIX and XXX respectively. For the biradical produced from epoxide (2), anti-clockwise rotation about C(1) - C(2) bond and cyclisation leads to the formation of sterically less hindered 1R,2S,3S,4S(1S,2R,3R,4R)- 2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (36). The isomeric product (37) which would be formed by



Scheme XXIX



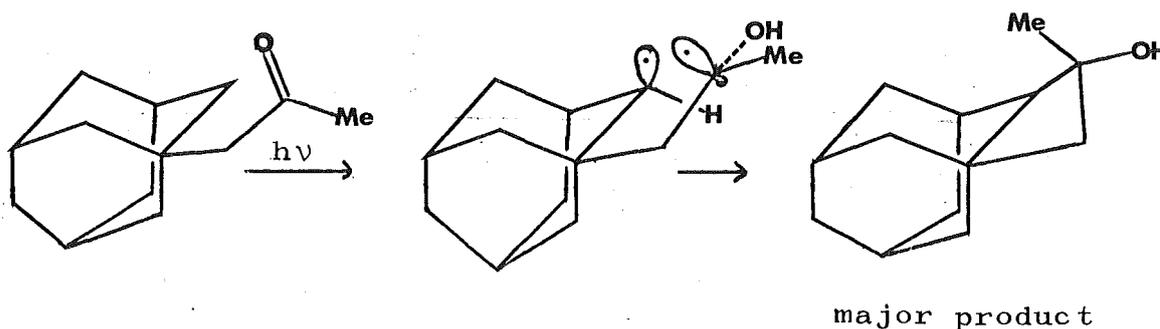
Scheme XXX

clockwise rotation about C(1)-C(2) bond was not observed, due to the unfavourable steric interaction between C(2) methyl and the adjacent C(1) phenyl.

The stereospecificity observed in this reaction contrasts with the photolysis of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1) where products of both clockwise and anti-clockwise rotation about the C(1)-C(2) bond of the intermediate biradical are observed. The preference for 1S,2S,3S(1R,2R,3R)-2,3-epoxy-1-phenyl-1-cyclobutanol (30) (cf. 1R,2S,3S(1S,2R,3R)-2,3-epoxy-1-phenyl-1-cyclobutanol (31)) of 1.67 : 1.00 was rationalised in terms of the steric compression being greater between the epoxide oxygen and phenyl than the epoxide and hydroxy. This preference factor which is steric in origin will be small until the C(1), C(4) bond is well developed and the groups in a proximate position. For epoxide (2) this steric effect is overweighted by the steric interaction of the C(1) and C(2) substituents, an interaction which is present not only when C(1) and C(4) are proximate.

The biradical formed by γ -hydrogen abstraction by the excited carbonyl of 2S,3R(2R,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanone (3) cyclises to give 1R,2R,3R,4S(1S,2S,3S,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (35). The isomer 1S,2R,3R,4S(1R,2S,3S,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (38) could not be detected. The steric interaction between methyl and phenyl again determines the

stereochemistry of product formation. The stereospecificity of epoxy-cyclobutanol formation for the methyl substituted epoxyketones (2) and (3) contrasts with that observed for 1-adamantylacetone⁷⁴ (Scheme XXXI) where rehybridisation of the carbonyl carbon

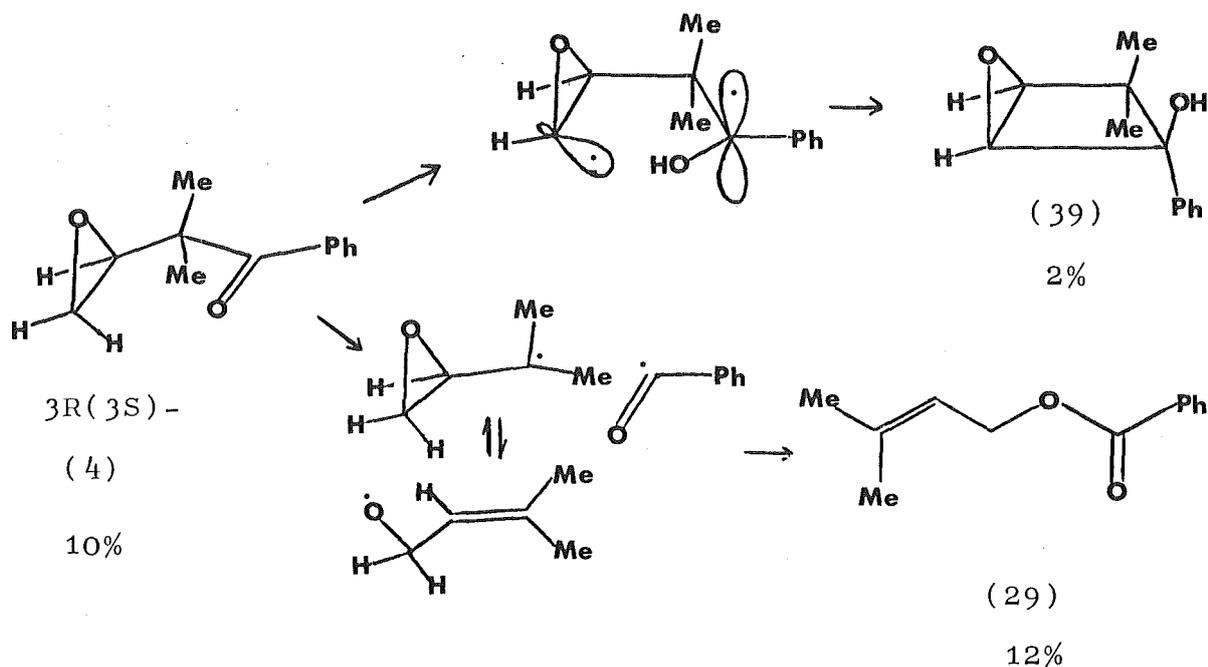


Scheme XXXI

from sp_2 to sp_3 , which must occur in cyclobutanol formation, is thought to occur simultaneously or immediately following γ -hydrogen abstraction. The rehybridised 1,4-biradical has a built in preference for closure to give the observed major product. The biradicals formed from the phenyl ketones (2) and (3) and from α -adamantylacetophenone⁴² by γ -hydrogen abstraction are however expected to be longer lived and rehybridisation in this way no longer controls the stereochemistry of product formation. Fragmentation of the 1,4-biradical intermediates formed from ketones (2) and (3) was unimportant since repeated attempts to isolate

1-phenyl-1-propanone and acetic acid were not successful. No products of α -cleavage were observed.

α -Cleavage becomes important in the photolysis of 3S(3R)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4). Photolysis of 3S(3R)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) in benzene gave three spots on an alumina tlc plate and chromatography at 0° afforded 3-methyl-2-buten-1-ol benzoate (29)⁷¹, 2,3-epoxy-4,4-dimethyl-1-phenyl-1-cyclobutanol (39) and starting material (4) in 12, 2 and 10% yields respectively (Scheme XXXII).



Scheme XXXII

3-Methyl-2-buten-1-ol benzoate (29) and 3,4-

epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) appeared as a single spot on tlc. The middle spot was isolated as a crystalline product and identified as 2,3-epoxy-4,4-dimethyl-1-phenyl-1-cyclobutanol (39) but repeated attempts to isolate the more polar product were not successful.

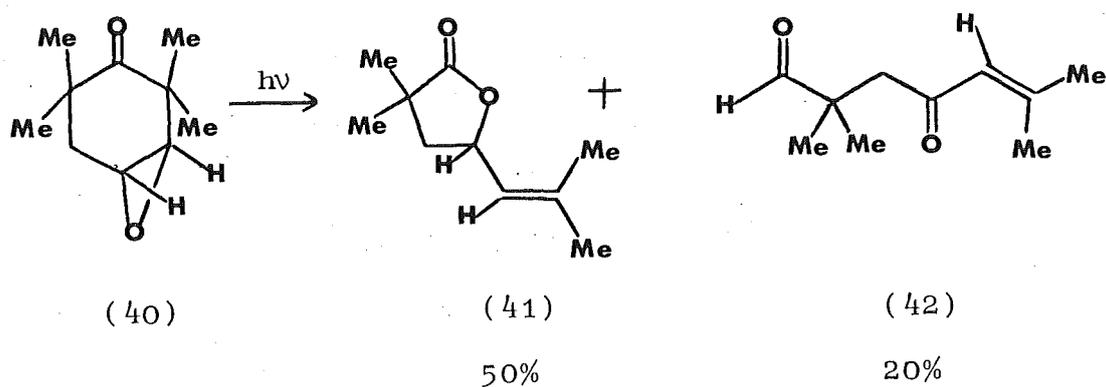
Photoproduct, 3-methyl-2-buten-1-ol benzoate (29)⁷¹ was isolated as a liquid and is isomeric with the starting ketone (4). The infrared spectrum (KBr) showed intense absorption at 1723 and 1259 cm^{-1} characteristic of an ester chromophore. The presence of a strong ultraviolet absorption at $\lambda_{\text{max}}^{\text{EtOH}}$ 229.2 nm ($\epsilon_{\text{max}} = 1.30 \times 10^4$) confirmed the presence of the conjugated ketone chromophore. The pmr spectrum showed the methyls as a singlet centred at δ 1.78, the methylene protons as a doublet (J 7.0 Hz) centred at δ 4.80 and the olefinic proton as a complex triplet (J 7.0 Hz) centred at δ 5.47 and coupled with the methyls. The doublet at δ 4.80 and the triplet at δ 5.47 were shown to be coupled by double irradiation techniques. Two clusters of peaks centred at δ 7.50 (3H's) and δ 7.97 (2H's) are characteristic of a phenyl group adjacent to a carbonyl chromophore. An authentic sample of 3-methyl-2-buten-1-ol benzoate (29) was synthesised by reaction of 1-bromo-3-methyl-2-butene with sodium benzoate in benzene.

2,3-Epoxy-4,4-dimethyl-1-phenyl-1-cyclobutanol (39) was only isolated in 2% yield. The pmr spectrum

of this compound showed the methyls as singlets at δ 0.60 and δ 1.00. The C(2)H and C(3)H centred at δ 4.17 and δ 3.57 respectively were coupled (J 2 Hz) to each other. The hydroxy appeared as a singlet at δ 2.68 and the aromatic protons were a multiplet ($W_{\frac{h}{2}}$ 3 Hz) centred at δ 7.27. The coupling constant (J 2 Hz) between C(2)H and C(3)H was similar to that observed for epoxycyclobutanols (30), (31), (35) and (36). The infrared spectrum in chloroform of 2,3-epoxy-4,4-dimethyl-1-phenyl-1-cyclobutanol (39) confirmed the presence of hydroxyl (3575 cm^{-1}) and aromatic (708 cm^{-1}) functions; however assignment of the stereochemistry could not be conclusively determined. The limited amount of compound available hindered further structural studies. By analogy with the photolysis of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1), rotation about C(1)-C(2) bond of the intermediate biradical of 4 (Scheme XXXII) would be expected to occur in a clockwise manner and result in the formation of the 1R,2S,3S(1S,2R,3R)-2,3-epoxy-4,4-dimethyl-1-phenyl-1-cyclobutanol (39). No other isomeric epoxycyclobutanols were observed in the reaction nor were any products of fragmentation of intermediate 1,4-biradical detected.

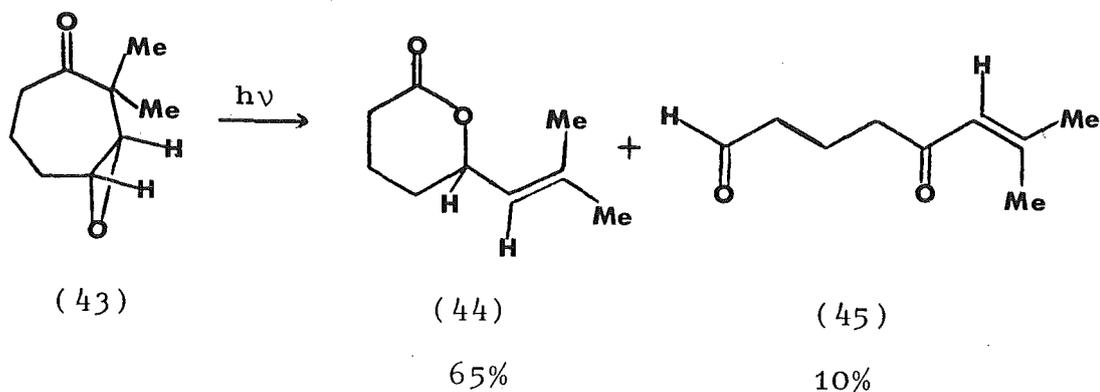
Lewis et al.^{37,45} in their study of methyl substituted butyrophenones observed a similar increase in the importance of α -cleavage with an increase in methyl substitution adjacent to the carbonyl. Murray

et al.⁷⁵ have reported the photolysis of 3,4-epoxy-2,2,6,6-tetramethylcyclohexanone (40) to give 5(2-methylprop-2-enyl)-3,3-dimethyl-1-oxacyclopentan-2-one (41) and 4-keto-2,2,6-trimethyl-5-heptenal (42) (Scheme XXXIII). The seven-membered



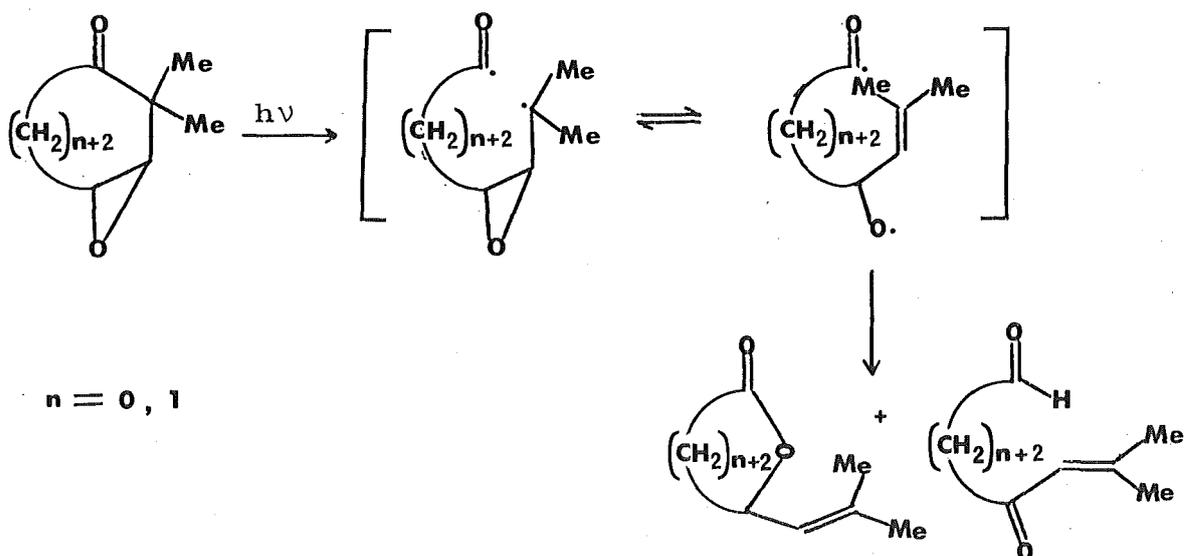
Scheme XXXIII

ring epoxyketone analogue 3,4-epoxy-2,2-dimethylcycloheptanone (43) gave on photolysis 6(2-methylprop-2-enyl)-1-oxacyclohexan-2-one (44) and 5-keto-7-methyl-6-octenal (45) (Scheme XXXIV). The formation



Scheme XXXIV

of these products from the photolysis of 3,4-epoxy-2,2,6,6-tetramethylcyclohexanone (40) and 3,4-epoxy-2,2-dimethyl cycloheptanone (43) is thought to involve initial α -cleavage of the excited ketones as shown in Scheme XXXV.



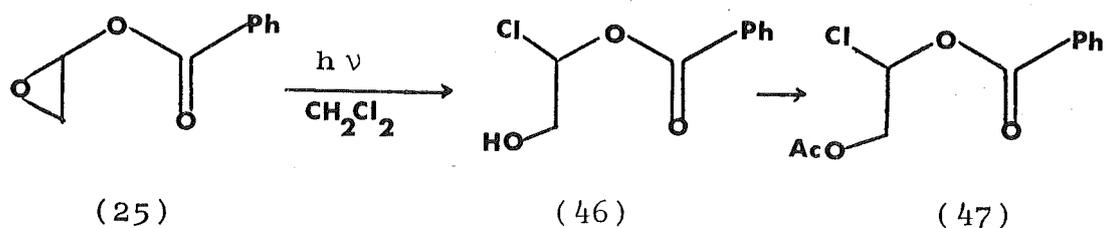
Scheme XXXV

The isolation of 3-methyl-2-buten-1-ol benzoate (29) from the photoreaction of 3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) is thought to occur by a similar pathway. The excited ketone undergoes α -cleavage to give benzoyl radical and the epoxyalkyl radical (Scheme XXXII). Electron redistribution in the epoxyalkyl radical followed by recombination with the benzoyl radical results in the formation of 3-methyl-2-buten-1-ol benzoate (29). Failure to detect benzaldehyde and 3-

methyl-2-butenal indicated that hydrogen abstraction by the benzoyl radical is not a competitive process. However, the low yield of photoproducts characterised suggests that extensive photodecomposition of the starting material occurs under the reaction conditions. The photochemical behaviour of 3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) contrasts markedly with that of 3,4-epoxy-1-phenyl-1-butanone (1), 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3). While γ -hydrogen abstraction and formation of epoxycyclobutanols is the dominant reaction process observed in the photolysis of epoxides (1), (2) and (3), the effect of the two alkyl substituents at C(2) facilitates α -cleavage which successfully competes with γ -hydrogen abstraction for epoxide (4). The increase in the proportion of the reaction proceeding by α -cleavage may result from either the increased stability of the epoxyalkyl radical or from increased steric strain between the C(1) and C(2) substituents in the starting epoxide (4). The formation of 3-methyl-2-buten-1-ol benzoate (29) is the first example of such a reaction for an acyclic β,γ -epoxyketone.

The effect on the course of photolysis of replacing the C(2) of 3,4-epoxy-1-phenyl-1-butanone (1) by oxygen was investigated by examining the photolysis of oxiranyl benzoate (25). The effect of three ultraviolet light sources (3000, 2537 and 1849 - 2537 $\overset{\circ}{\text{A}}$)⁷² were examined. When this compound was photolysed with

3000 Å and 2537 Å ultraviolet lamps, no reaction could be detected by tlc and pmr spectrum analysis. Prolonged photolysis under these conditions led to a gradual decomposition of the starting material. When oxiranyl benzoate (25) was dissolved in anhydrous dichloromethane and photolysed with 1849 - 2537 Å ultraviolet lamps in a quartz vessel for 8 hours, 1-chloro-2-hydroxyethyl benzoate (46) could be isolated (Scheme XXXVI). The infrared spectrum indicated the presence



Scheme XXXVI

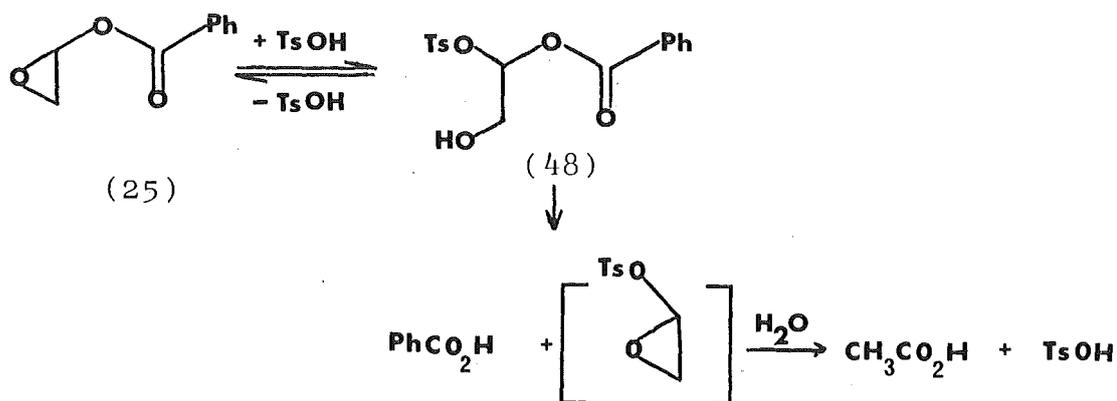
of an aromatic ester (1742, 1250 and 714 cm^{-1}) and hydroxyl (3450 cm^{-1}) functions. The pmr spectrum showed the hydroxyl proton as a singlet at $\delta 4.87$. The $\text{C}(2)\text{H}_2$ was a doublet ($J 5.5\text{ Hz}$) centred at $\delta 4.05$ and coupled with the $\text{C}(1)\text{H}$ which appeared as a triplet centred at $\delta 6.72$. The aromatic protons absorbed in the region $\delta 7.34 - 8.20$. The assignment of the product as 1-chloro-2-hydroxyethyl benzoate (46) and not 2-chloro-1-hydroxyethyl benzoate was determined by conversion to the acetate. The pmr spectrum of the

acetylated product (47) showed that the methylene doublet had been deshielded to a greater extent (δ 4.05 to δ 4.56) than the methine triplet (δ 6.72 to δ 6.82). This demonstrates that the hydroxyl group of 46 is bonded to C(2) and not C(1). The product is envisaged to arise by ground state addition of hydrochloric acid produced from dichloromethane under the reaction conditions to the epoxide (25). The absence of any photoreaction of oxiranyl benzoate (25) under normal photolysis conditions may be because reverse γ -hydrogen transfer competes with cyclisation and elimination occurring from an initially produced 1,4-biradical. Alternatively there may be an increase in the importance of the $\pi \rightarrow \pi^*$ triplet for the ester chromophore which may be lower in energy than the $n \rightarrow \pi^*$ triplet state.

A similar reaction to that observed when the photolysis was carried out in dichloromethane was observed when oxiranyl benzoate (25) was reacted with p-toluenesulphonic acid in anhydrous ether (Scheme XXXVII). The product 2-hydroxy-1-tosyloxyethyl benzoate (48) was highly unstable and decomposed to give a mixture from which benzoic acid and p-toluenesulphonic acid could be isolated. The identity of compound (48) followed from its pmr spectrum which showed the aromatic methyl as a sharp singlet at δ 2.20, the C(2)H₂ as a doublet (J 4.5 Hz) centred at δ 3.90 and coupled with the C(1)H which appeared as a

triplet (J 4.5 Hz) centred at δ 6.88. The hydroxyl proton was a broad singlet centred at δ 3.28 and the aromatic protons were a multiplet between δ 7.10 - 8.23. The pmr spectrum after acetylation showed the methylene protons were deshielded (δ 3.90 cf. δ 4.58) more than the methine proton (δ 6.88 cf. δ 6.85) by the introduction of the acetate group.

The hydroxytoluenesulphonate (48) arises by addition of toluenesulphonic acid to the epoxide with the nucleophile attacking C(1). No product involving attack of nucleophile at C(2) was detected, consistent with the expected mode of addition of an acid to an unsymmetrical epoxide. Decomposition of the tosylate (48) is thought to occur as shown in Scheme XXXVII. The tosylate (48) could lose p-toluenesulphonic acid to give oxiranyl benzoate (25)



Scheme XXXVII

or by loss of benzoic acid give an epoxide intermediate which would react with traces of water to give p-toluenesulphonic acid and acetic acid.

The photolysis of 2,3-epoxy-3-methyl-1-butanol benzoate (28) in benzene or pentane was examined with 3000 Å, 2537 Å and 1849 - 2537 Å ultraviolet lamps but no photochemical reaction could be detected.

The unreactivity of the epoxy esters, oxiranyl benzoate (25) and 2,3-epoxy-3-methyl-1-butanol benzoate (28) with light is in marked contrast with the photolysis of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1), 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3) where epoxycyclobutanol formation is dominant and with 3S(3R)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) where α -cleavage and formation of 3-methyl-2-buten-1-ol benzoate (29) competes with cyclobutanol formation.

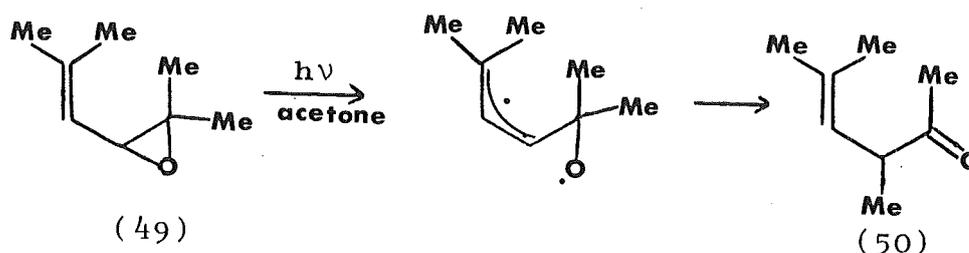
A notable feature of the photochemical reactions of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1), 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3) was the absence of significant quantities of products formed by fragmentation of the 1,4-biradicals produced by γ -hydrogen abstraction. This contrasts with the photolysis of 1-phenyl-1-alkanone^{37,45} and its derivatives where fragmentation is often the major reaction process. The expected high energy of oxirene^{76,77} which would be a transitory product⁴⁹ for such a process

for epoxides (1), (2) and (3) probably accounts for the marked preference for cyclobutanol formation. Photolysis of 1-alkyl analogues of epoxides (1), (2) and (3) where the reaction might be expected to occur more rapidly from the excited singlet state could increase the importance of the fragmentation process. Photolysis⁴⁹ of 3S,4S(3R,4R)-3,4-epoxy-1,4-diphenyl-1-butanone where the phenyl substituent at C(4) is capable of stabilising an adjacent radical gives a higher but still only modest yield of products resulting from fragmentation. The effect of radical stabilising substituents at C(3) and at C(3) and C(4) is a subject for further investigation but if substrates could be found which favour fragmentation it may be possible to generate oxirene and its derivatives at very low temperatures for spectroscopic studies.

APPENDIX I

Photolysis of 4,5-Epoxycholest-2-enes

Only a limited amount of information is known about the photochemistry of 3,4-epoxyolefins^{78,79}. In most cases studied, the primary photoproducts have been β, γ -unsaturated ketones, many of which undergo further reactions. The mechanism proposed for the formation of β, γ -unsaturated ketones involves initial sensitisation of the epoxyolefin chromophore by a suitable sensitiser (e.g. acetone), followed by a homolytic C-O bond cleavage to form a biradical which is stabilised by participation of the alkene. 1,2-Migration of an alkyl or hydrogen group occurs to give the observed product. This process is shown in Scheme XXXVIII for 4,5-epoxy-2,5-dimethyl-2-hexene (49) which on photolysis⁸⁰ has been shown to give 3,5-dimethyl-4-hexen-2-one (50). Although 1,2-shifts



Scheme XXXVIII

are not common in photochemistry, analogy may be found in the photoreactions of styrene oxide⁸¹ and indene oxide⁷⁹ which rearrange in the presence of light to give phenylethanal and 2-indanone respectively.

The present study involves the photolysis of 4 α ,5-epoxy-5 α -cholest-2-ene (51) and its epimer 4 β ,5-epoxy-5 β -cholest-2-ene (52). 4 α ,5-Epoxy-5 α -cholest-2-ene (51) was obtained⁸² in 75% yield from the solvolysis of the tosylate of 4 α ,5-epoxy-5 α -cholestan-3 α -ol in collidine and the epimer 4 β ,5-epoxy-5 β -cholest-2-ene (52) was prepared⁸² in low yield (24%) from treatment of the tosylate of 4 β ,5-epoxy-5 β -cholestan-3 β -ol by heating under reflux in DMF containing LiCO₃.

Photolysis of an acetone solution of 4 α ,5-epoxy-5 α -cholest-2-ene (51) with 3000 Å lamps for 10 hours resulted in the isolation of a crystalline photoproduct identified as A-nor-B-homo-5 β -cholest-2-en-6-one (53) (mp 83 - 4°) in 60% yield. The infrared spectrum of this compound showed the presence of a carbonyl moiety contained in a seven-membered ring by an absorption of ν_{\max} 1709 cm⁻¹. The lack of an intense absorption in the ultraviolet region (λ 230 - 260 nm) confirmed the absence of a conjugated ketone chromophore. In the pmr spectrum the two olefinic protons of C(2) and C(3) were complex and were centred at δ 5.55 and δ 5.90 respectively. A broad singlet at δ 3.58 is assigned as the C(5 β)H

markedly deshielded by alkene and carbonyl moieties. The molecular ion in the mass spectrum (M^+ 384.3403) is consistent with a molecular formula $C_{27}H_{44}O$. The compound exhibited a negative optical rotatory dispersion (α -66), and molecular models of this ketone are consistent with this negative value. The structure of this unsaturated ketone (53) was further confirmed by hydrogenation in the presence of palladium on carbon (5%) as catalyst to A-nor-B-homo-5 β -cholestan-6-one (54)⁸³ (mp 93 - 4°) and by conversion to an unsaturated alcohol by reaction with lithium aluminium hydride. The pmr spectrum of the A-nor-B-homo-5 β -cholestan-6-one (54) exhibited two singlets at δ 0.70 and δ 1.07 identified as the $C(18)H_3$ and $C(19)H_3$ respectively, and a doublet of doublets (J 8 Hz, J' 5 Hz) centred at δ 3.02 was assigned to the $C(5\beta)H$. The infrared spectrum indicated a strong carbonyl absorption at 1709 cm^{-1} and the negative optical rotatory dispersion (α -79) (Figure X) was consistent with

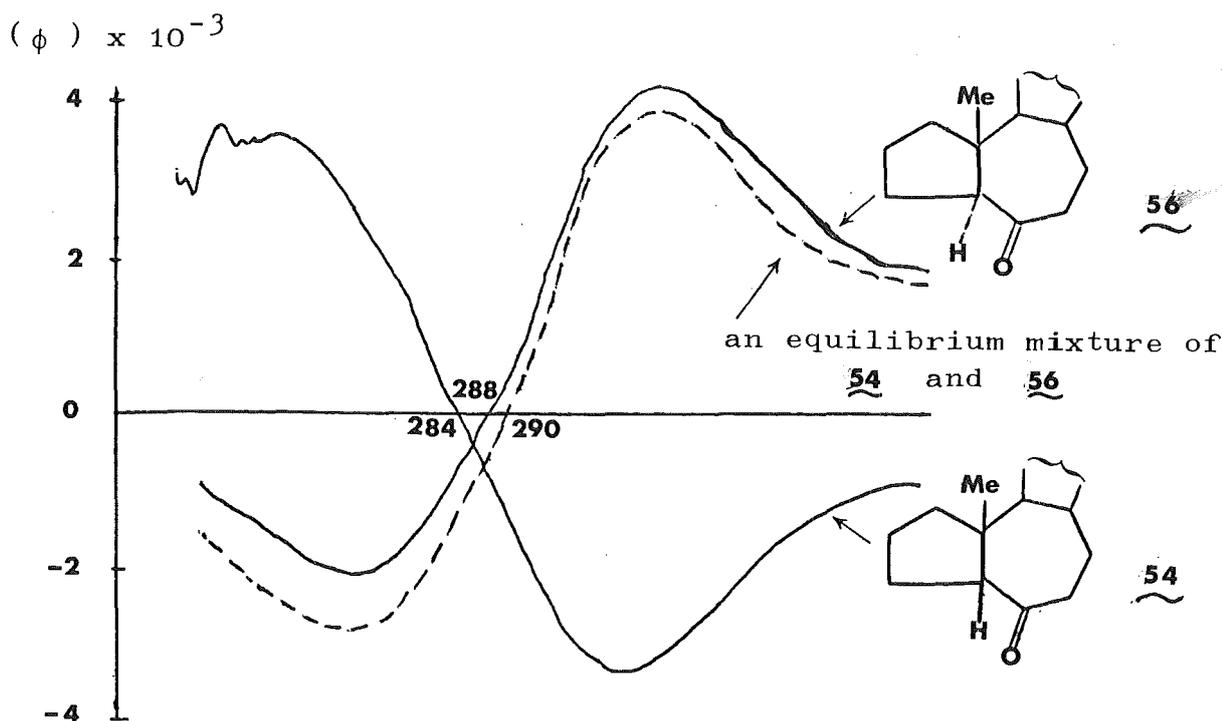
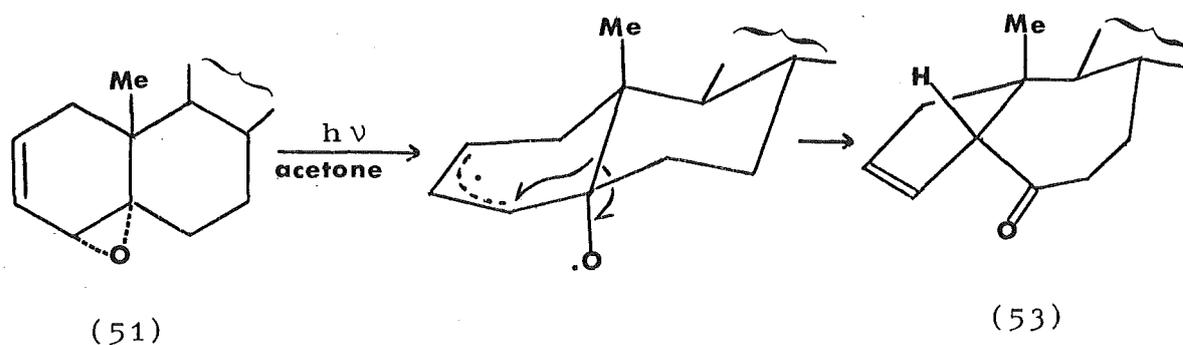


Figure X

prediction based on molecular models. The mass spectrum indicated a molecular ion at 386.3544 consistent with a molecular formula $C_{27}H_{46}O$. The compound exhibited similar spectral characteristics to those reported by Nussim.⁸³ Reaction of A-nor-B-homo-5 β -cholestan-6-one (54) with aqueous sulphuric acid (20%) in dioxane for 2 hours at 100° gave an equilibrium mixture of A-nor-B-homo-5 β - and 5 α -cholestan-6-ones (54) and (56). The equilibrium was biased towards the thermodynamically more stable A-nor-B-homo-5 α -cholestan-6-one (56) whose pmr spectrum indicated the two angular methyls to absorb at $\delta 0.67$ (lit. value, $\delta 0.67$ (C(18)H₃), $\delta 0.67$ (C(19)H₃)). An ethanol solution of the equilibrium mixture of ketones gave a positive optical rotatory dispersion ($\alpha +70$) (Figure X) (lit. value⁸³, $\alpha +88$). The equilibrium ratio of A-nor-B-homo-5 α - and 5 β -cholestan-6-ones has been previously determined⁸³ to be 4 : 1 in favour of the more stable 5 α - isomer (56).

The structure of A-nor-B-homo-5 β -cholest-2-en-6 α -ol formed by lithium aluminium hydride reduction of A-nor-B-homo-5 β -cholest-2-en-6-one (53) was determined by the presence of an hydroxyl absorption at 3423 cm^{-1} in the infrared spectrum. The pmr spectrum indicated the presence of two olefinic protons as multiplets at $\delta 5.45$ (1H) and $\delta 5.84$ (1H). The C(5 β)H was a singlet at $\delta 2.47$ and C(6 β)H a complex doublet (J 10 Hz) centred at $\delta 4.00$.

The formation of photoproduct A-nor-B-homo-5 β -cholest-2-en-6-one (53) on photolysis of 4 α ,5-epoxy-5 α -cholest-2-ene (51) is thought to arise by acetone sensitised excitation of the olefin epoxide and cleavage of the C-O bond to give the allylic biradical (Scheme XXXIX). Rearrangement involving β -face migration of C(10)-C(5) bond to C(4) as shown results in the formation of A-nor-B-homo-5 β -cholest-2-en-6-one (53). Photoepimerisation of photoproduct (53) was not observed.

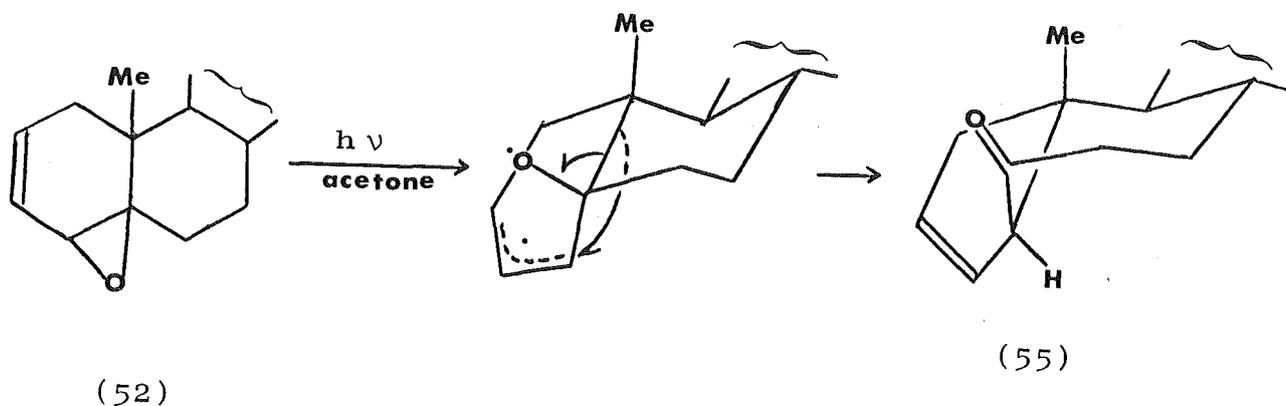


Scheme XXXIX

An analogous photoreaction was also observed for 4 β ,5-epoxy-5 β -cholest-2-ene (52) which on photolysis in acetone solution gave a reaction mixture from which A-nor-B-homo-5 α -cholest-2-en-6-one (55) could be isolated by rapid chromatography. The pmr spectrum in deuteriochloroform showed the two olefinic protons centred at δ 5.80 and the tertiary C(5 α)H as a multiplet centred at δ 3.88. The infrared spectrum indicated by a strong absorption

at 1709 cm^{-1} the presence of a carbonyl moiety in a seven-membered ring. The structure of this compound was also confirmed by conversion to A-nor-B-homo-5 α -cholestan-6-one (56) whose pmr spectrum indicated the C(18)H₃ and C(19)H₃ both centred at $\delta 0.67$ (lit. value⁸³ $\delta 0.67$ (C(18)H₃), $\delta 0.67$ (C(19)H₃)). The spectrum was identical in all respects with the compound obtained from the acid catalysed isomerisation of A-nor-B-homo-5 β -cholestan-6-one (54). The infrared spectrum has an intense carbonyl absorption at 1704 cm^{-1} (lit. value 1703 cm^{-1}) and the compound gave a positive optical rotatory dispersion. The amplitude ($\alpha +66$) was smaller than the literature value ($\alpha +136$), probably due to the presence of impurities in the photolysis sample.

The formation of A-nor-B-homo-5 α -cholest-2-en-6-one (55) from photolysis of epoxide (52) followed a similar mechanism (Scheme XXXX) as shown for 4 α ,5-epoxy-5 α -cholest-2-ene (51). The reaction



Scheme XXXX

differs however in that α -face migration of C(10)-C(5) bond to C(4) results in the formation of the 5 - isomer (55).

The photolysis of $4\alpha,5$ -epoxy- 5α - and $4\beta,5$ -epoxy- 5β -cholest-2-enes (51) and (52) to give A-nor-B-homo- 5β - and - 5α -cholest-2-en-6-ones (53) and (55) respectively is the first report of photo-reactions of α,β -unsaturated steroid epoxides. The yield of A-nor-B-homo- 5β cholest-2-en-6-one (53) from irradiation of $4\alpha,5$ -epoxy- 5α -cholest-2-ene (51) makes this a viable route to C(3) and in particular C(2) substituted A-nor-B-homo-C(6)-ketones.

EXPERIMENTAL

Photolysis was carried out in a Rayonet Photochemical Reactor (manufactured by the Southern New England Ultraviolet Company, Connecticut, U.S.A., Cat. No. RPR-100). The compound to be photolysed was dissolved in either anhydrous benzene, acetone or dichloromethane, and the solution degassed by suction and flushed with dry oxygen-free nitrogen. Photolysis was carried out under a nitrogen atmosphere and the reaction followed by drawing successive aliquots to examine by thin layer chromatography or proton magnetic resonance spectroscopy.

Melting points are uncorrected. Infrared spectra were recorded on a Shimadzu IR-27G spectrometer for liquid films, chloroform or carbon tetrachloride solutions, ultraviolet spectra on a Shimadzu MPS-50L for ethanol solutions, optical rotatory dispersion on a Jasco ORD/UV-5 and pmr spectra on a Varian A60 or T60 spectrometer for deuterated chloroform solutions with chloroform and tetramethylsilane as internal standards. Mass spectra were recorded on an A.E.I. MS902 spectrometer. Alumina used for chromatography was Spence Grade H. "5% Deactivated alumina" refers to Grade H to which 5% V/V of 10% acetic acid

has been added. Silica gel (Sorbsil, B.S.C. Grade) and dry column alumina (Brockmann Act. III/20 mm); and silica (Brockmann Act. III/30 mm) were also used where appropriate.

All solvents used were purified and redistilled as followed: Ether was dried and distilled over sodium hydride and stored over sodium wire. Dichloromethane was washed with sulphuric acid (conc), water, saturated sodium chloride and dried over calcium chloride in that order and distilled and stored over 5A molecular sieves. Acetone was dried with anhydrous potassium carbonate followed by distillation from phosphorous pentoxide. Petroleum ether was distilled from phosphorous pentoxide. Reagent grade benzene was stirred with sulphuric acid (conc) (80 cc of acid per 1000 cc of benzene) washed with water, aqueous sodium bicarbonate, dried over magnesium sulphate, distilled from lithium aluminium hydride and stored over sodium wire. Pyridine was purified by distillation of reagent grade from potassium hydroxide pellets. Chromium trioxide was ground and stored in a vacuum desiccator over phosphorous pentoxide prior to use.

1S(1R)-1-Phenyl-3-buten-1-ol (5)

Freshly distilled 1-bromo-2-propene (48 g) in dry ether (60 cc) was added dropwise to a vigorously stirred solution of magnesium filings (10 g)

in dry ether (225 cc) at -10° , under a nitrogen atmosphere (the reaction may be initiated by addition of a crystal of iodine). The solution was stirred for a further 2 hours. A solution of benzaldehyde (40 g, analytical grade) in dry ether (60 cc) was added dropwise and the reaction kept at -10° with constant stirring for 2 hours. Saturated ammonium chloride solution was carefully added and ^{the} product extracted with ether. The organic phase was dried with magnesium sulphate and concentrated to give 1S(1R)-1-phenyl-3-buten-1-ol (5) which was purified by vacuum distillation (110° , 10 mm Hg). (32 g), pmr⁵⁸ (CDCl₃) δ 2.40 (s, 1, OH), δ 2.55 (d of d, J 6.5 Hz, J' 6.5 Hz, 2, C(2)H₂), δ 4.73 (t, J 6.5 Hz, 1, C(1)H), δ 4.85 - 6.18 (m, 3, C(3)H and C(4)H₂), δ 7.32 (m, $\frac{h}{2}$ 2 Hz, 5, C₆H₅); ν_{\max}^{film} 3425, 1605, 1592, 1498, 1458, 926, 765, 707 cm⁻¹; $\lambda_{\max}^{\text{MeOH}}$ 253.8nm (ϵ 215), 256.7 (ϵ 236), 263.5 (ϵ 179); mass spectrum M⁺ 148.0882 (calc. for C₁₀H₁₂O, 148.0888).

3,4-Epoxy-1-phenyl-1-butanol (6)

To a solution of meta-chloroperbenzoic acid (31.5 g) in anhydrous ether (1000 cc) was added 1S(1R)-1-phenyl-3-buten-1-ol (5) (21 g). The reaction was kept at room temperature for 13 $\frac{1}{2}$ days. Solid potassium carbonate was added to neutralise the remaining peracid. The mixture was then filtered through an alumina column and distillation (30° , 30 mm Hg) gave crude product which was further purified by column

chromatography on 5% deactivated alumina. Elution with petroleum ether - ether (10:2) gave the 3,4-epoxy-1-phenyl-1-butanols (6) (16 g), pmr (CDCl_3) δ 1.88 (m, $W_{\frac{h}{2}}$ 14 Hz, 2, C(2)H₂), δ 2.28 - 3.50 (m, 3, C(3)H and C(4)H₂), δ 3.22 (broad s, $W_{\frac{h}{2}}$ 13 Hz, 1, OH), δ 4.80 (m, $W_{\frac{h}{2}}$ 13 Hz, 1, C(1)H), δ 7.28 (m, $W_{\frac{h}{2}}$ 2 Hz, 5, C₆H₅); $\nu_{\text{max}}^{\text{film}}$ 3460, 1500, 1460, 1055, 840, 760 and 710 cm^{-1} ; $\lambda_{\text{max}}^{\text{MeOH}}$ 251nm (ϵ 173), 257.5 (ϵ 200), 263.7 (ϵ 150); mass spectrum M^+ 164.0833 (calc. for C₁₀H₁₂O₂, 164.0837), $M^+ - \text{H}_2\text{O}$ 146.0735 (146.0732).

3S(3R)-3,4-Epoxy-1-phenyl-1-butanone (1)

Chromium trioxide⁶⁰ (2.0 g) was added to a stirred solution of redistilled anhydrous pyridine (3.16 g) in a round bottom flask fitted with a drying tube. The reaction mixture was stirred for 20 minutes. A solution of the 3,4-epoxy-1-phenyl-1-butanols (6) (0.54 g), in a minimum amount of dichloromethane (1 cc) was added to the complex. A black tar was formed immediately and the reaction was left stirring for a half hour. The liquid layer was decanted from the black tar, which was extracted with two volumes of ether (2 x 20 cc). The organic phase was washed with 2% sodium bicarbonate solution and with water until no pyridine smell could be detected. The ether layer was then dried over magnesium sulphate and distilled under reduced pressure (30 mm Hg) at room temperature to give 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1) (0.43 g), pmr (CDCl_3)

δ 2.55 (d of d, J 5 Hz, J' 2.5 Hz, 1, C(4)H trans to C(3)H), δ 2.87 (d of d, J 5 Hz, J' 4 Hz, 1, C(4)H cis to C(3)H), δ 3.10 - 3.60 (m, $W_{\frac{h}{2}}$ 30 Hz, 3, C(3)H and C(2)H₂), δ 7.50 (m, 3, aromatic protons), δ 7.90 (m, 2, aromatic protons); ν_{\max}^{film} 3100 - 2900, 1686, 1600, 1584, 1452, 1203 and 697 cm⁻¹; $\lambda_{\max}^{\text{EtOH}}$ 243 nm (ϵ 2.44 x 10⁴), 279 (ϵ 1.08 x 10³), 328 (ϵ 57). The sample decomposes in the source outlet of the mass spectrometer.

Decomposition of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone

(1)

On standing at 0° for 3-4 months, 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1) rearranged to give 4-hydroxy-1-phenyl-2-buten-1-one (8) which was crystallised from methanol as needles, mp 69 - 71°, pmr (CDCl₃) δ 2.08 (s, $W_{\frac{h}{2}}$ 13 Hz, 1, OH), δ 4.50 (d, J 2 Hz, 2, C(4)H₂), δ 7.20 (m, $W_{\frac{h}{2}}$ 2 Hz, 2, C(2)H and C(3)H), δ 7.33 - 8.13 (m, 5, C₆H₅); $\nu_{\max}^{\text{CHCl}_3}$ 3475, 1672, 1623 cm⁻¹; $\lambda_{\max}^{\text{EtOH}}$ 257.2 nm (ϵ 2.2 x 10⁴); mass spectrum M⁺ 162.0675 (calc. for C₁₀H₁₀O₂, 162.0681). Treatment of this product with a trace of HCl (conc) in methanol afforded 2-phenylfuran (7)⁶², pmr (CDCl₃) δ 6.45 (d of d, J 2 Hz, J' 4 Hz, 1, C(3)H), δ 6.65 (d, J 2 Hz, 1, C(2)H), δ 7.20 - 7.71 (m, 6, C(4)H and C₆H₅). This data compares well with the literature values; pmr (CDCl₃) δ 6.45 (d of d, J 2 Hz, J' 4 Hz, 1, C(3)H), δ 6.62 (d, J 2 Hz, 1, C(2)H) δ 7.20 - 7.70 (m, 5, C₆H₅), δ 7.45 (m, 1, C(4)H). 2-Phenylfuran (7) was also obtained in the attempts to distil 3S(3R)-3,4-epoxy-

1-phenyl-1-butanone (1) by heating in the presence of traces of pyridine at 60° under vacuum.

Reaction of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1) with HCl (conc) in methanol

Treatment of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1) with HCl (conc) in methanol for 2 hours gave a reaction mixture from which 2-phenylfuran (7) (39%), pmr (CDCl₃) δ 6.45 (d of d, J 2 Hz, J' 4 Hz, 1, C(3)H), δ 6.65 (d, J 2 Hz, 1, C(2)H), δ 7.20 - 7.71 (m, 6, C(4)H and C₆H₅) and one other product (56%) thought to be 4-chloro-3-hydroxy-1-phenyl-1-butanone or its isomer 3-chloro-4-hydroxy-1-phenyl-1-butanone could be isolated, pmr (CDCl₃) δ 3.27 (m, 3, OH and C(4)H₂), δ 3.60 (d, J 7 Hz, 2, C(2)H₂), δ 4.35 (m, 1, C(3)H), δ 7.45 (m, 3, aromatic protons), δ 7.75 (m, 2, aromatic protons); $\nu_{\text{max}}^{\text{film}}$ 3460, 1690, 1600, 1593, 750 and 685 cm⁻¹; mass spectrum M⁺ (198), M⁺-H₂O (180), M⁺-C₃H₆OCl (105) and M⁺-C₄H₆O₂Cl (77) (calc. for C₁₀H₁₁O₂Cl³⁵, 198).

Photolysis of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1)

Photolysis was carried out in a Rayonet photo-reactor using 3000 Å ultraviolet lamps⁷². A solution of 3S(3R)-3,4-epoxy-1-phenyl-1-butanone (1) (0.125 g) in anhydrous benzene (125 cc) in a pyrex vessel fitted with a two-necked adaptor, one of which was connected to a water condenser and the other was stoppered,

was degassed under suction for half an hour. Nitrogen gas was flushed through this solution repeatedly to ensure the solution was oxygen-free. The free end of the condenser was then sealed off by a balloon containing nitrogen gas. The pressure inside the reaction vessel was brought to atmospheric pressure by momentarily releasing the stopper and deflating the balloon.

The progress of the photoreaction was monitored by tlc (silica) using chloroform as developing solvent. After 19 hours, photolysis was stopped and the benzene solvent removed by vacuum distillation (30° , 20 mm Hg), and the residue adsorbed onto 5% deactivated alumina. Elution with petroleum ether - ether (10:1) gave 1S, 2S, 3S(1R, 2R, 3R)-2,3-epoxy-1-phenyl-1-cyclobutanol (30), (0.06 g), pmr (CDCl_3) (Figure III) δ 2.92 (s, $W_{\frac{h}{2}}$ 3 Hz, 1, OH), δ 2.02 (d of d, J 12.5 Hz, J' 2.5 Hz, 1, C(4)H_a), δ 2.50 (d, J 12.5 Hz, 1, C(4)H_b), δ 3.97 (m, 2, C(2)H and C(3)H), δ 7.33 (m, $W_{\frac{h}{2}}$ 22 Hz, 5, C₆H₅); $\nu_{\text{max}}^{\text{CCl}_4}$ 3600, 3530, 1500, 1455, 1195, 1143, 1070, 840, 770, 710 and 628 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 252.2 nm (ϵ 234.7), 258.5 (ϵ 237.8), 265.0 (ϵ 171.6); mass spectrum M^+ 162.0674 (calc. for C₁₀H₁₀O₂, 162.0681). Further elution with petroleum ether : ether (10:2) gave 1R, 2S, 3S(1S, 2R, 3R)-2,3-epoxy-1-phenyl-1-cyclobutanol (31), (0.035 g) recrystallised from methanol, mp $54 - 5^{\circ}$, pmr (CDCl_3) δ 2.02 (s, $W_{\frac{h}{2}}$ 12 Hz, 1, OH), δ 2.27 (m, $W_{\frac{h}{2}}$ 3 Hz, 2, C(4)H_a and C(4)H_b), δ 3.90 (m, $W_{\frac{h}{2}}$ 3 Hz, 2, C(2)H and C(3)H), δ 7.30 (m, $W_{\frac{h}{2}}$ 5 Hz, 5, C₆H₅); $\nu_{\text{max}}^{\text{CCl}_4}$ 3620, 3475, 1503, 1454, 1194, 1135, 1090, 850, 773, 710 and 600 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 252.0 nm (ϵ 185),

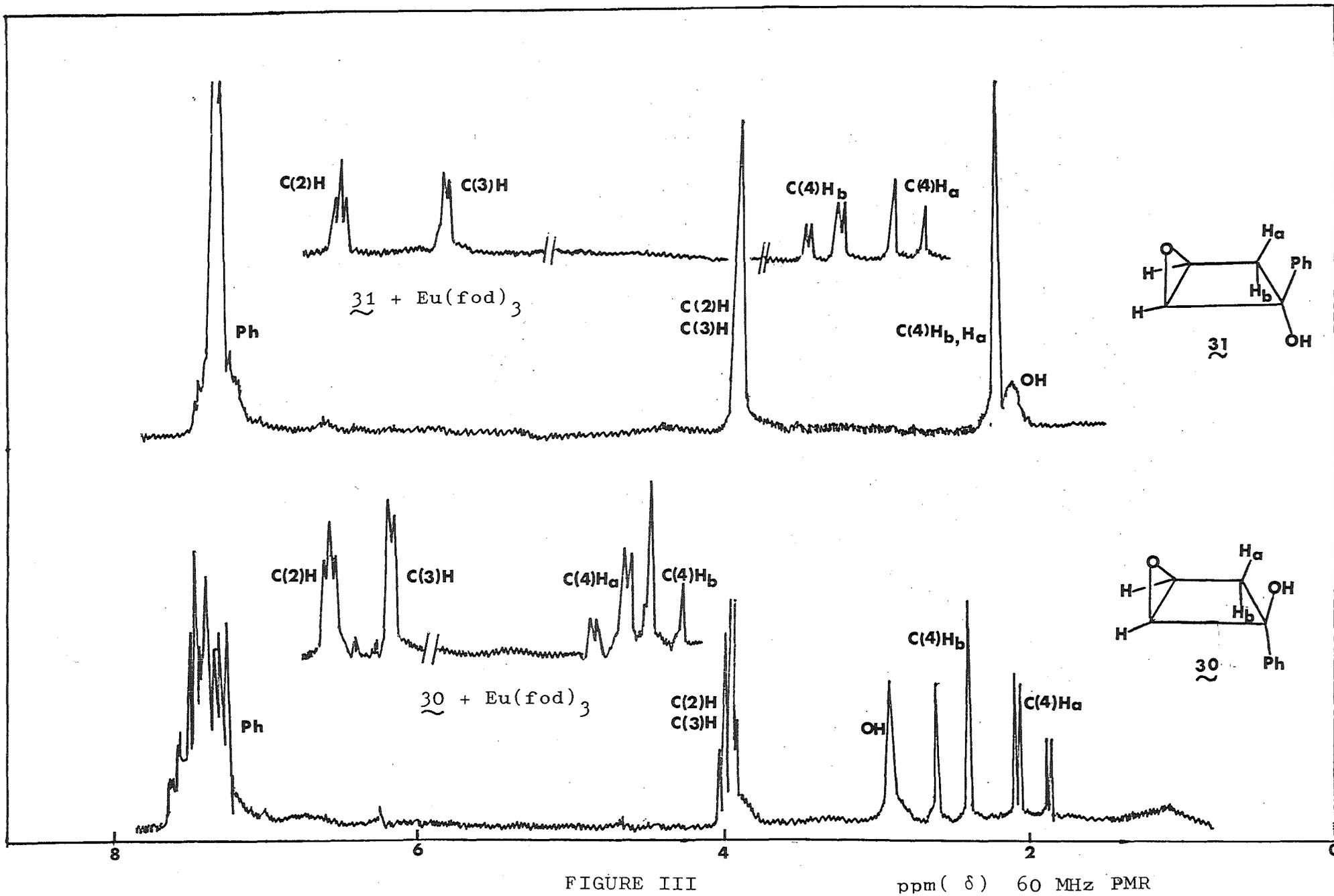


FIGURE III

ppm (δ) 60 MHz PMR

258.0 (205), 264.4 (151.3); mass spectrum M^+ 162.0679 (calc. for $C_{10}H_{10}O_2$, 162.0681). Pmr dilution studies in carbon tetrachloride showed the chemical shift of hydroxyl proton in compound (30) was less influenced by dilution than that of compound (31) (Figure IV).

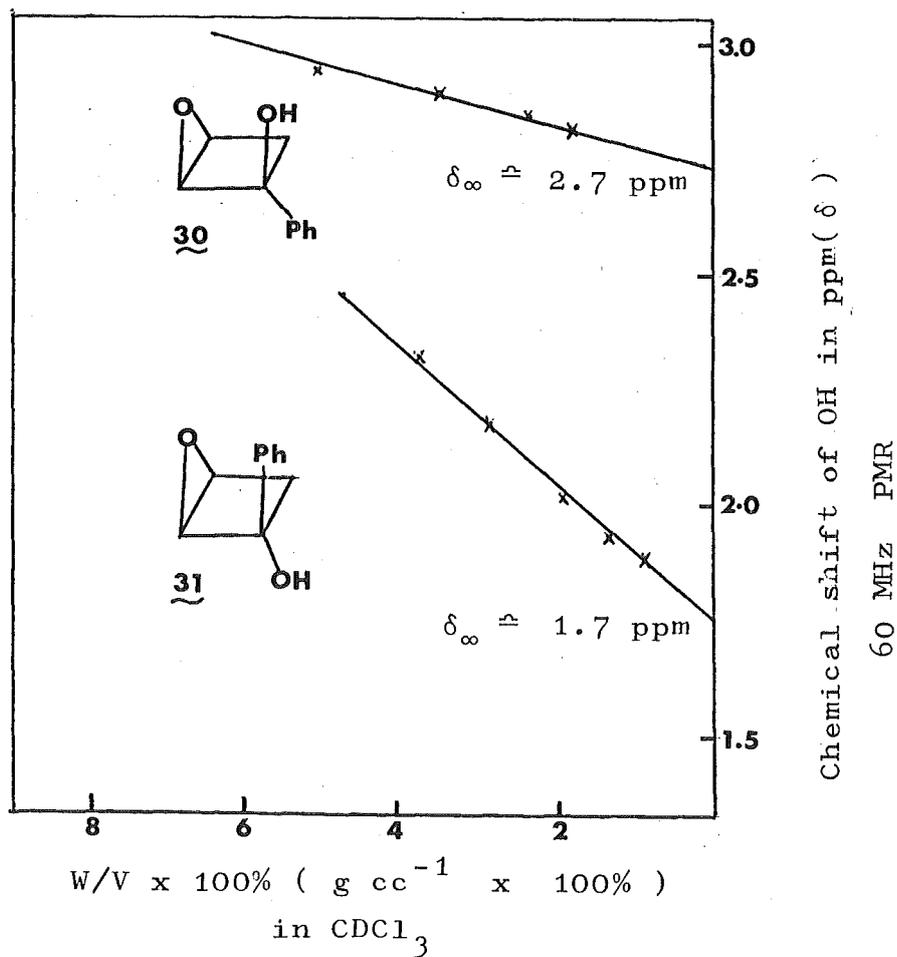


FIGURE IV

Acetophenone was detected by glc (carbowax 20 M, chromosorb G, 2½%) in 2% yield. The pmr spectrum of the crude reaction mixture did not have a peak corresponding to acetophenone but the concentration was outside the detectable range.

1S,2S(1R,2R)- and 1R,2S(1S,2R)- 2-Methyl-1-phenyl-3-buten-1-ols (9) and (10)

The organo-magnesium Grignard reagent formed from 1-bromo-2-butene (4 g) was allowed to react with benzaldehyde (1.4 g) in ether (60 cc) at -10° for two hours. A saturated solution of ammonium chloride was carefully added to the reaction mixture. The product was extracted with ether and after removal of solvent was adsorbed onto 5% deactivated alumina (100 g). Elution with petroleum ether - ether (10:2) gave 3,5-dimethyl-4-phenyl-1,6-heptadien-4-ol (11) (0.1 g), pmr (CDCl_3) δ 0.89 (d, J 7 Hz, 6, C(3)- and C(5)- CH_3 's), δ 2.25 (s, 1, OH), δ 2.80 (d of q, J 8 Hz, J' 7 Hz, 2, C(3)H and C(5)H), δ 4.90 - 6.00 (m, 6, C(1) H_2 , C(2)H, C(6)H and C(7) H_2), δ 7.33 (m, $W_{\frac{h}{2}}$ 3 Hz, 5, C_6H_5); $\nu_{\text{max}}^{\text{film}}$ 3600, 2978, 1450, 1360, 1008, 918, 773 and 715 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 247.2 nm (ϵ 168), 252.0 (ϵ 175), 258.0 (ϵ 210), 264.3 (ϵ 161); mass spectrum M^+ 216 (calc. for $\text{C}_{15}\text{H}_{20}\text{O}$, 216). Further elution with petroleum ether - ether (10:4) gave a mixture^{64,65} (31.5:50.5) of 1S,2S(1R,2R)- and 1R,2S(1S,2R)- 2-methyl-1-phenyl-3-buten-1-ols (9) and (10) (2.2 g), ν_{max} 3440, 2983, 1497, 1457, 1023, 918, 770 and 710 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 247.8 nm (ϵ 109), 252.5 (ϵ 153), 258.4 (ϵ 190), 264.5 (ϵ 144) which on repeated column chromatography on 5% deactivated alumina gave 1S,2S(1R,2R)-2-methyl-1-phenyl-3-buten-1-ol (9), pmr (CDCl_3) δ 0.83 (d, J 6 Hz, 3, C(2) CH_3), δ 2.12 (s, $W_{\frac{h}{2}}$ 6 Hz, 1, OH), δ 2.48 (m, $W_{\frac{h}{2}}$ 32 Hz, 1, C(2)H), δ 4.37 (d, J 8 Hz, 1, C(1)H),

δ 5.00 - 6.15 (m, 3, C(3)H and C(4)H₂), δ 7.30 (m, $W_{\frac{h}{2}}$ 3 Hz, 5, C₆H₅), and 1R,2S(1S,2R)-2-methyl-1-phenyl-3-buten-1-ol (10), pmr (CDCl₃) δ 0.97 (d, J 6 Hz, 3, C(2)CH₃), δ 2.22 (s, 1, OH), δ 2.42 (m, $W_{\frac{h}{2}}$ 32 Hz, 1, C(2)H), δ 4.50 (d, J 6 Hz, 1, C(1)H), δ 4.80 - 6.00 (m, 3, C(3)H and C(4)H₂), δ 7.30 (m, $W_{\frac{h}{2}}$ 3 Hz, 5, C₆H₅).

1S,2R,3R(1R,2S,3S)-, 1S,2R,3S(1R,2S,3R)-, 1R,2R,3S(1S,2S,3R)- and 1R,2R,3R(1S,2S,3S)- 3,4-Epoxy-2-methyl-1-phenyl-1-butanols (12), (13), (14) and (15)

A solution of 1S,2S(1R,2R)- and 1R,2S(1S,2R)-2-methyl-1-phenyl-3-buten-1-ols (9) and (10) (3.0 g) and meta-chloroperbenzoic acid (4.5 g) in ether (200 cc) was kept at room temperature for 8 days. The solution was washed with saturated potassium carbonate, dried with anhydrous magnesium sulphate and after removal of solvent afforded a mixture of the isomeric 3,4-epoxy-2-methyl-1-phenyl-1-butanols (12), (13), (14) and (15) (2.5 g), ν_{\max} 3455, 2980, 1498, 1457, 1250, 1195, 1025, 923, 893, 833, 772, 760 and 712 cm⁻¹;
 $\lambda_{\max}^{\text{EtOH}}$ 247.9 nm (ϵ 147), 252.5 (ϵ 184), 258.2 (ϵ 215), 269.3 (ϵ 156), 268.0 (ϵ 95); pmr (CDCl₃) 1S,2R,3R(1R,2S,3S)- (12) δ 0.71 (d, J 7 Hz, C(2)CH₃), δ 1.85 (m, $W_{\frac{h}{2}}$ 40 Hz, C(2)H), δ 2.17 (m, $W_{\frac{h}{2}}$ 60 Hz, C(3)H and C(4)H₂), δ 4.62 (d, J 7 Hz, C(1)H), δ 7.30 (m, $W_{\frac{h}{2}}$ 3 Hz, C₆H₅);
 1S,2R,3S(1R,2S,3R)- (13) δ 0.82 (d, J 7 Hz, C(2)CH₃), δ 1.85 (m, $W_{\frac{h}{2}}$ 40 Hz, C(2)H), δ 2.17 (m, $W_{\frac{h}{2}}$ 60 Hz, C(3)H and C(4)H₂), δ 4.48 (d, J 7 Hz, C(1)H), δ 7.30 (m, C₆H₅);
 1R,2R,3S(1S,2S,3R)- (14) δ 1.03 (d, J 6 Hz, C(2)CH₃),

δ 1.85 (m, $W_{\frac{h}{2}}$ 40 Hz, C(2)H), δ 2.17 (m, $W_{\frac{h}{2}}$ 60 Hz, C(3)H and C(4)H₂), δ 4.65 (d, J 6 Hz, C(1)H), δ 7.30 (m, C₆H₅); 1R,2R,3R(1S,2S,3S)- (15) δ 0.84 (d, J 7 Hz, C(2)CH₃), δ 1.85 (m, $W_{\frac{h}{2}}$ 40 Hz, C(2)H), δ 2.17 (m, $W_{\frac{h}{2}}$ 60 Hz, C(3)H and C(4)H₂), δ 4.90 (d, J 6 Hz, C(1)H), δ 7.30 (m, C₆H₅); mass spectrum M⁺ 178.0998 (calc. for C₁₁H₁₄O₂, 178.0994). Repeated chromatography on 5% deactivated alumina afforded pure samples of 1S,2R,3R(1R,2S,3S)- and 1R,2R,3R(1S,2S,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanols (12) and (15), the most polar and the least polar isomers respectively.

Reaction of a sample of 1S,2S(1R,2R)-2-methyl-1-phenyl-3-buten-1-ol (9) (0.03 g) with meta-chloroperbenzoic acid gave a 1:2 mixture of 1S,2R,3R(1R,2S,3S)- and 1S,2R,3S(1R,2S,3R)- 3,4-epoxy-2-methyl-1-phenyl-1-butanols (12) and (13) (0.03 g), pmr (CDCl₃) δ 0.71 (d, J 7 Hz) and δ 0.82 (d, J 7 Hz) respectively. A similar reaction of 1R,2S(1S,2R)-2-methyl-1-phenyl-3-buten-1-ol (10) gave a 1:1 mixture of 1R,2R,3S(1S,2S,3R)- and 1R,2R,3R(1S,2S,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanols (14) and (15), pmr (CDCl₃) δ 1.03 (d, J 6 Hz) and δ 0.84 (d, J 7 Hz) respectively.

1S,2S,3S(1R,2R,3R)-2-Methyl-1-phenyl-1,3-butanediol (16)

To a solution of 1S,2R,3R(1R,2S,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanol (12) (0.08 g) in anhydrous ether (10 cc) was added lithium aluminium hydride (0.08 g) in ether (10 cc). The reaction mixture was

left stirring for 12 hours. Sodium sulphate crystals were added until a white sludge was obtained. The organic layer was decanted and after removal of the solvent, the residue was adsorbed onto a dry column of silica (100 g). Elution with chloroform and extraction of a band from the column gave 1S,2S,3S(1R,2R,3R)-2-methyl-1-phenyl-1,3-butanediol (16) (0.07 g), pmr (CDCl_3) δ 0.53 (d, J 7 Hz, 3, C(2)CH₃), δ 1.20 (d, J 7 Hz, 3, C(4)H₃), δ 1.75 (m, $W_{\frac{h}{2}}$ 40 Hz, 1, C(2)H), δ 3.93 (s, $W_{\frac{h}{2}}$ 2 Hz, 2, C(1)OH and C(3)OH), δ 3.83 (m, $W_{\frac{h}{2}}$ 50 Hz, 1, C(3)H), δ 4.50 (d, J 9 Hz, 1, C(1)H), δ 7.33 (m, $W_{\frac{h}{2}}$ 3 Hz, 5, C₆H₅).

4S,5S,6S(4R,5R,6R)-4,5-Dimethyl-6-phenyl-1,3-dioxacyclohexan-2-one (17)

Sodium metal (0.02 g) was added to a mixture of 1S,2S,3S(1R,2R,3R)-2-methyl-1-phenyl-1,3-butanediol (16) (0.07 g) and diethyl carbonate⁶⁷ (0.05 g) in anhydrous benzene (2 cc). The mixture was stirred and heated under reflux for one hour. Benzene containing ethanol, a by-product of the reaction, was carefully distilled from the reaction mixture. An additional volume of benzene (10 cc) was added and distillation continued until a further volume of benzene (5 cc) was removed.

The reaction mixture was then washed with three volumes of water (3 x 10 cc.), dried with anhydrous calcium chloride and the solvent removed

by distillation to give 4S,5S,6S(4R,5R,6R)-4,5-dimethyl-6-phenyl-1,3-dioxacyclohexan-2-one (17) (0.08 g). Extensive pmr decoupling experiments were carried out to obtain the coupling constants, pmr (CDCl₃) δ 0.80 (d, J 6.5 Hz, 3, C(5)CH₃), δ 1.45 (d, J 6.5 Hz, 3, C(4)CH₃), δ 1.93 (m, $W_{\frac{h}{2}}$ 40 Hz, 1, C(5)H), δ 4.37 (d of q, J 10.5 Hz, J' 6.5 Hz, 1, C(4)H), δ 4.95 (d, J 11.0 Hz, 1, C(6)H), δ 7.40 (m, $W_{\frac{h}{2}}$ 3 Hz, 5, C₆H₅); ν_{\max}^{film} 3000, 1755, 1500, 1458, 1397, 1368, 1341, 1252, 1198, 1118, 1072, 769 and 709 cm⁻¹; mass spectrum M⁺ 206.0946 (calc. for C₁₂H₁₄O₃, 206.0943).

1R,2S,3S(1S,2R,3R)-2-Methyl-1-phenyl-1,3-butanediol (18)

To a solution of 1R,2R,3R(1S,2S,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanol (15) (0.2 g) (containing approximately 5% of epoxyalcohol (14) as impurity) in ether (20 cc) was added lithium aluminium hydride (0.15 g) in ether (20 cc) and the resulting mixture was stirred for 12 hours. The product was isolated in the usual manner to give 1R,2S,3S(1S,2R,3R)-2-methyl-1-phenyl-1,3-butanediol (18) (0.11 g), pmr (CDCl₃) δ 0.72 (d, J 7 Hz, 3, C(2)CH₃), δ 1.17 (d, J 6 Hz, 3, C(4)H₃), δ 1.75 (m, $W_{\frac{h}{2}}$ 36 Hz, 1, C(2)H), 3.72 (m, $W_{\frac{h}{2}}$ 36 Hz, 1, C(3)H), δ 3.95 (s, $W_{\frac{h}{2}}$ 3 Hz, C(1)OH and C(3)OH), δ 5.02 (d, J 3.5 Hz, 1, C(1)H), δ 7.30 (m, $W_{\frac{h}{2}}$ 3 Hz, 5, C₆H₅).

4S,5S,6R(4R,5R,6S)-4,5-Dimethyl-6-phenyl-1,3-dioxacyclohexan-2-one (19)

To a solution of 1R,2S,3S(1S,2R,3R)-2-methyl-1-phenyl-1,3-butanediol (18) (0.10 g) and diethyl carbonate (0.07 g) in anhydrous benzene (2 cc) was added sodium metal and the resulting mixture heated under reflux for one hour. A few drops of benzene containing ethanol were carefully distilled from the reaction mixture and an additional volume of benzene (5 cc) added. Distillation was continued until a further volume (2 cc) of solvent was removed. The remaining solution was washed with water, dried with anhydrous calcium chloride and after removal of solvent gave 4S,5S,6R(4R,5R,6S)-4,5-dimethyl-6-phenyl-1,3-dioxacyclohexan-2-one (19) (0.11 g), pmr (CDCl₃) δ 0.84 (d, J 7.0 Hz, 3, C(5)CH₃), δ 1.45 (d, J 7.0 Hz, 3, C(4)CH₃), δ 2.23 (m, $W\frac{h}{2}$ 40 Hz, 1, C(5)H), δ 4.42 (m, $W\frac{h}{2}$ 28 Hz, 1, C(4)H), δ 5.57 (d, J 4.5 Hz, 1, C(6)H), δ 7.38 (m, $W\frac{h}{2}$ 3 Hz, 5, C₆H₅); $\nu_{\text{max}}^{\text{film}}$ 3001, 1751, 1501, 1456, 1397, 1367, 1251, 1200, 1119, 1077, 770 and 710 cm⁻¹.

2S,3S(2R,3R)- and 2S,3R(2R,3S)-3,4-Epoxy-2-methyl-1-phenyl-1-butanones (2) and (3)

Chromium trioxide⁶⁰ (1.5 g) was added to a stirred solution of redistilled dry pyridine (2.38 g) in dichloromethane (40 cc). After 20 minutes, a solution of 1S,2R,3R(1R,2S,3S)-, 1S,2R,3S(1R,2S,3R)-,

1R,2R,3S(1S,2S,3R)- and 1R,2R,3R(1S,2S,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanols (12), (13), (14) and (15) (0.5 g) in dichloromethane (2 cc) was added. The mixture was left stirring for 30 minutes. The product was extracted with ether which was washed with aqueous sodium bicarbonate solution (2%) and water. The ether layer was dried over anhydrous magnesium sulphate and the solvent removed by distillation to give a mixture of 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3) (0.45 g), ν_{\max}^{film} 2984, 1685, 1603, 1583, 1455, 1210, 979, 909, 849 and 712 cm^{-1} ; $\lambda_{\max}^{\text{EtOH}}$ 243.0 nm ($\epsilon 1.23 \times 10^4$), 279.0 ($\epsilon 1.04 \times 10^3$), 327.0 ($\epsilon 77$); mass spectrum M^+ 176.0843 (calc. for $C_{11}H_{12}O_2$, 176.0837); pmr ($CDCl_3$) 2S,3S(2R,3R)- (2), δ 1.38 (d, J 7 Hz, C(2)CH₃), δ 2.72 (m, $W_{\frac{h}{2}}$ 26 Hz, C(4)H₂), δ 3.25 (m, $W_{\frac{h}{2}}$ 20 Hz, C(2)H and C(3)H), δ 7.47 and 8.00 (m, C₆H₅); 2S,3R(2R,3S)- (3) δ 1.26 (d, J 7 Hz, C(2)CH₃), δ 2.72 (m, $W_{\frac{h}{2}}$ 26 Hz, C(4)H₂), δ 3.25 (m, $W_{\frac{h}{2}}$ 20 Hz, C(2)H and C(3)H), δ 7.48 and 7.95 (m, C₆H₅).

Oxidation of a sample of 1S,2R,3R(1R,2S,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanol (12) (0.03 g) afforded 2S,3R(2R,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanone (3) (0.03 g), pmr ($CDCl_3$) δ 1.26 (d, J 7 Hz). Similar oxidation of 1R,2R,3R(1S,2S,3S)-3,4-epoxy-2-methyl-1-phenyl-1-butanol (15) (0.08 g) afforded the same epoxy ketone (3) (0.07 g), pmr ($CDCl_3$) δ 1.26 (d, J 7 Hz). Oxidation of a mixture (1:1) of 1S,2R,3R(1R,2S,3S)- and 1S,2R,3S(1R,2S,3R)- 3,4-epoxy-2-methyl-1-phenyl-1-butanols (12) and (13) gave a mixture (1:1).

of 2S,3R(2R,3S)- and 2S,3S(2R,3R)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (3) and (2) respectively, pmr (CDCl₃) δ 1.26 (d, J 7 Hz) and δ 1.38 (d, J 7 Hz) respectively.

Photolysis of 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3)

A mixture of 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3) (0.27 g, $\underline{2} : \underline{3} = 2 : 1$) in anhydrous benzene (270 cc) was photolysed for 18 hours under the same conditions as employed in the photolysis of 3,4-epoxy-1-phenyl-1-butanone (1). After the removal of solvent under vacuum, the residue was adsorbed onto deactivated alumina (10 g). Elution with petroleum ether gave a 1 : 15 mixture of 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3) (0.06 g), pmr δ 1.38 (J 7 Hz) and δ 1.26 (J 7 Hz). Further elution with petroleum ether - ether (5 : 1) gave 1R,2R,3R,4S (1S,2S,3S,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (35), (0.02 g) which was crystallised from methanol as needles, m p 84 - 5^o, pmr (CDCl₃) (Figure V) δ 0.98 (d, J 8 Hz, 3, C(4)CH₃), δ 2.65 (q, J 8 Hz, 1, C(4)H), δ 2.85 (s, 1, C(1)OH), δ 3.98 (d, J 2 Hz, 1, C(3)H), δ 4.13 (d, J 2 Hz, 1, C(2)H), δ 7.40 (m, 5, C₆H₅). The chemical shift of the C(1)OH on extrapolation to infinite dilution absorbed at δ 2.8 (Figure VIII);
 ν_{\max} 3580, 1453, 1185, 990, 937, 841 and 708 cm⁻¹;

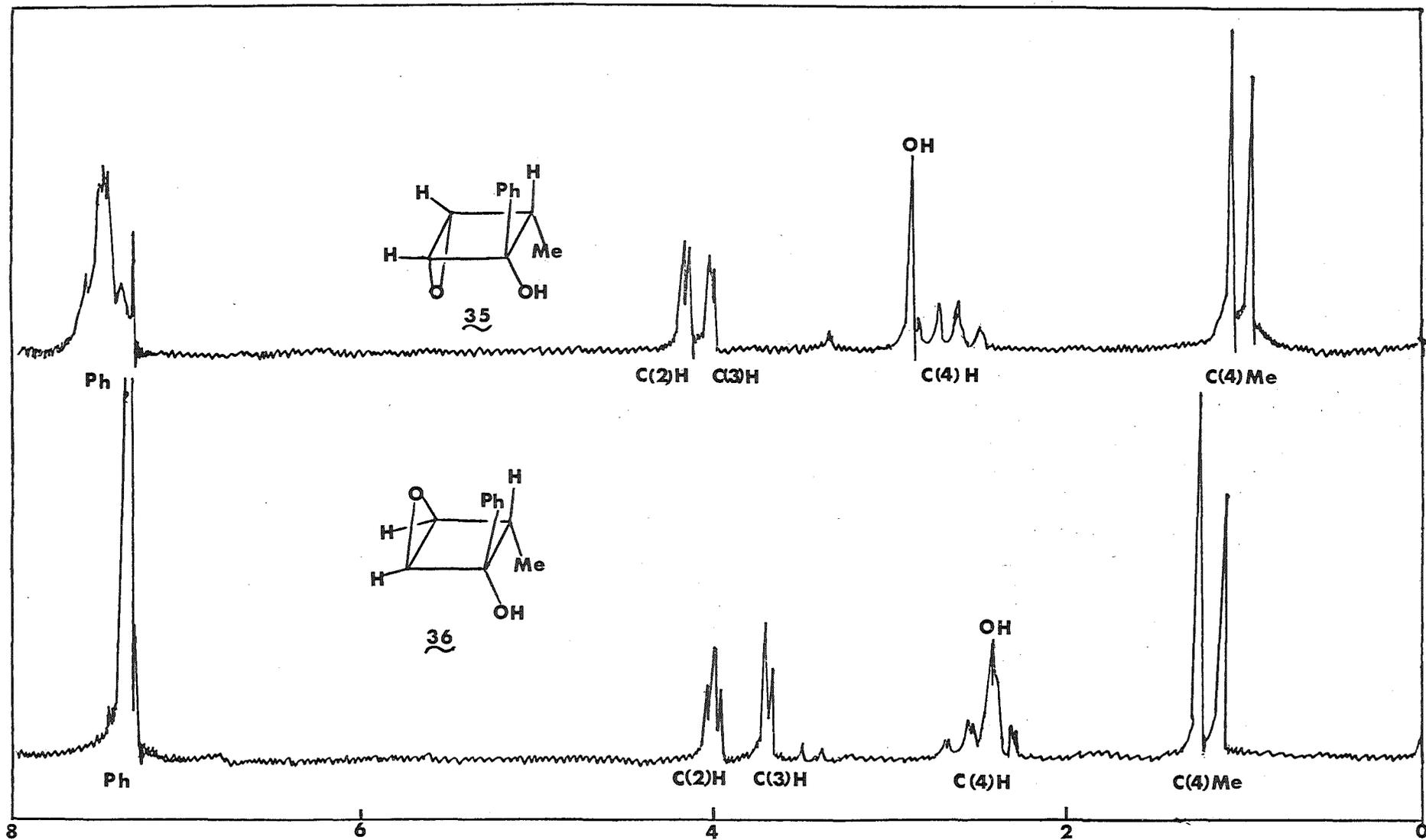
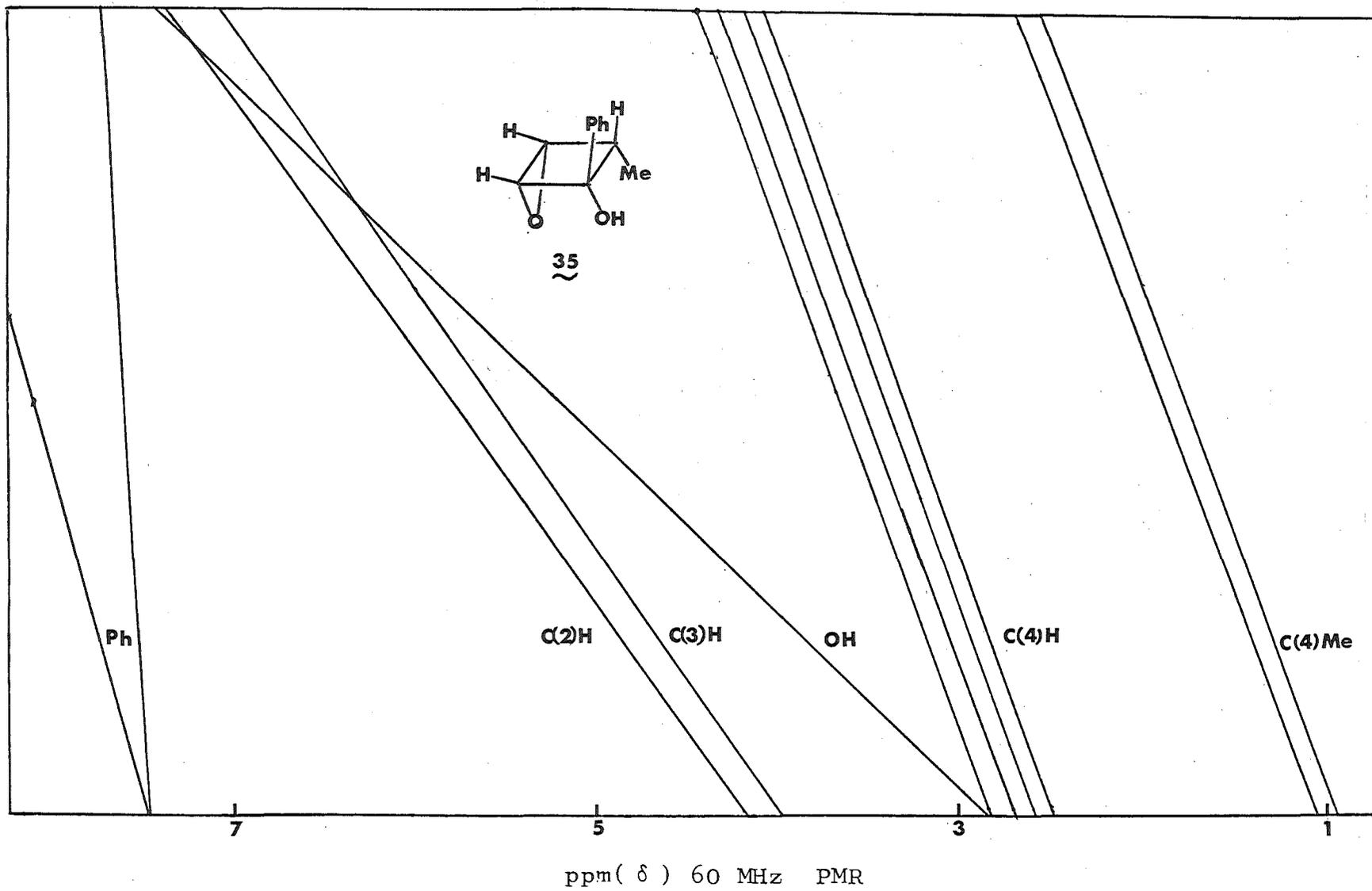
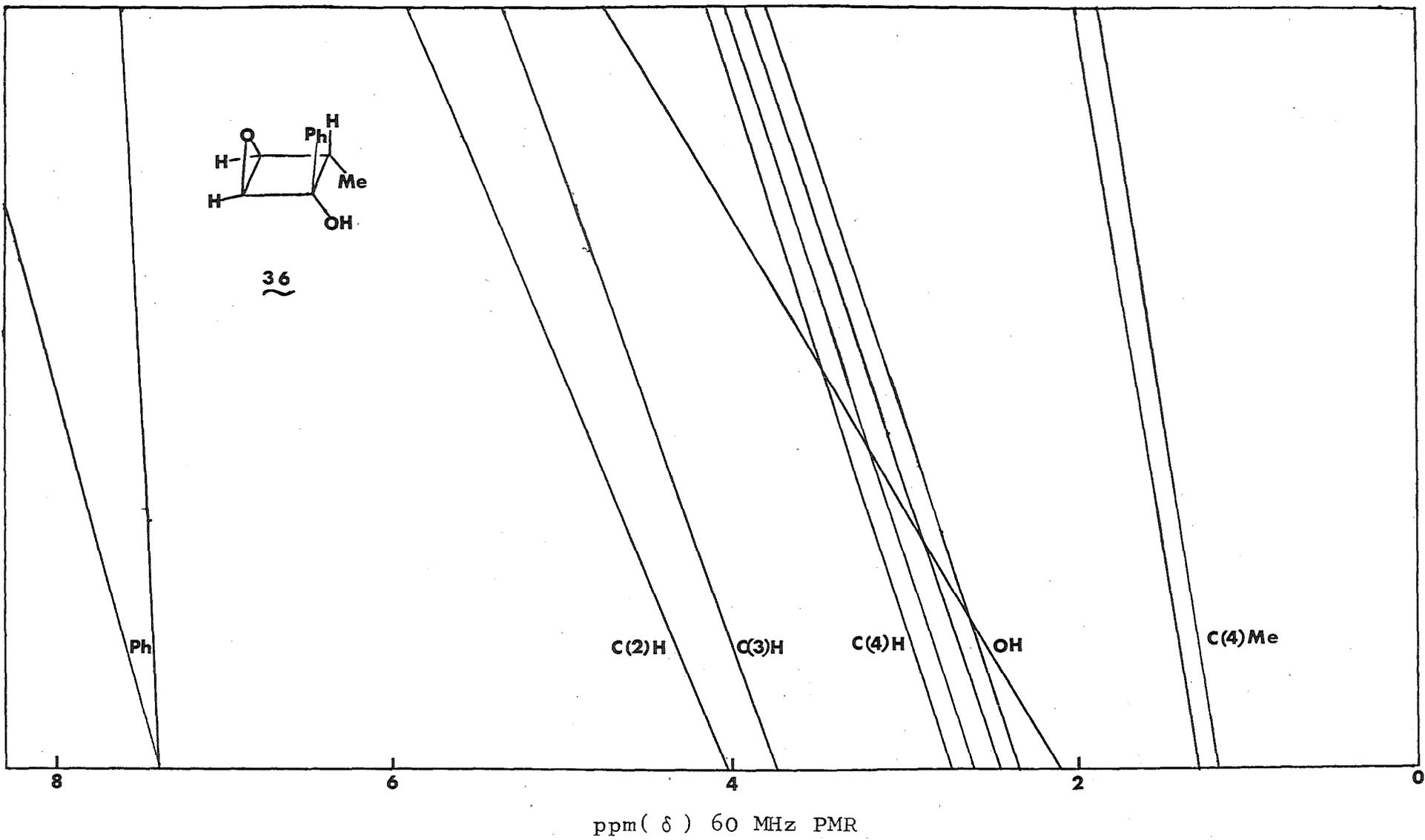


FIGURE V ppm(δ) 60 MHz PMR

Concentration of $\text{Eu}(\text{fod})_3$
FIGURE VI



Concentration of $\text{Eu}(\text{fod})_3$
FIGURE VII



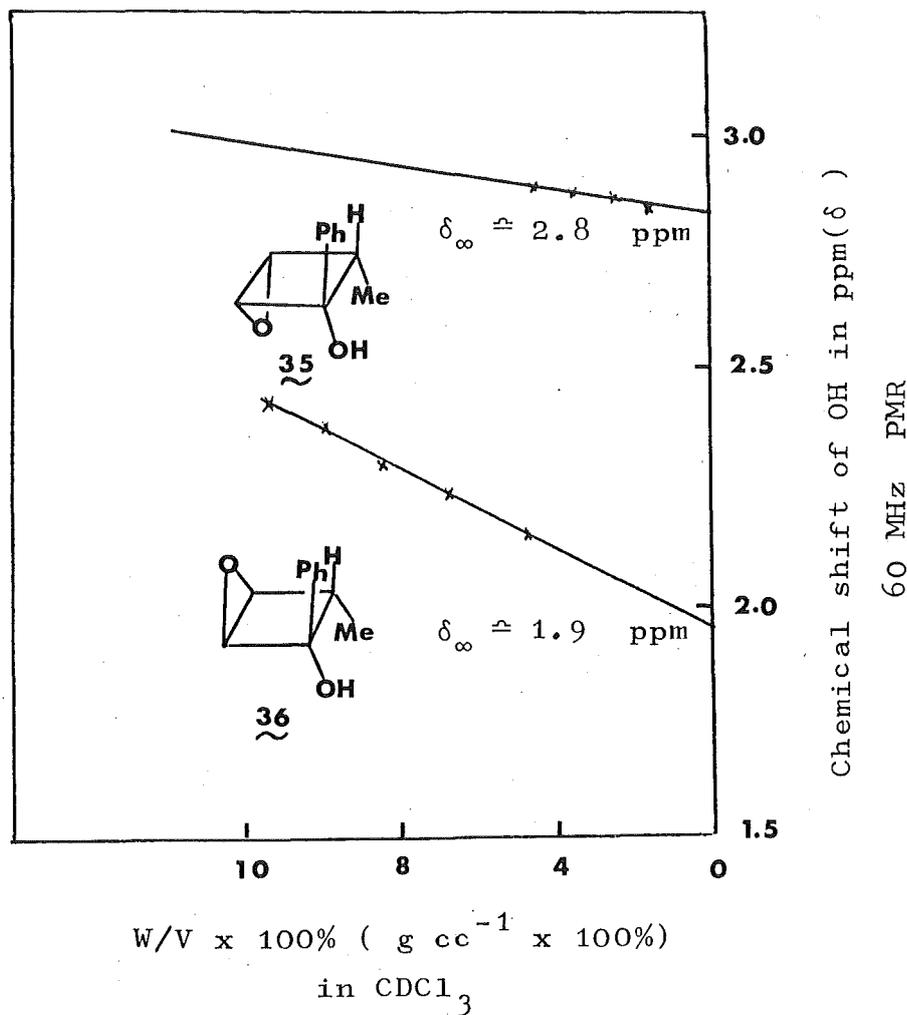


FIGURE VIII

$\lambda_{\text{max}}^{\text{EtOH}}$ 248 nm (ϵ 260), 252.0 (ϵ 280), 258.8 (ϵ 280), 265.0 (ϵ 207), 269.0 (ϵ 146); mass spectrum M^+ 176.0837 (calc. for $C_{11}H_{12}O_2$, 176.0837. Further elution with petroleum ether - ether (5 : 1) gave 1R,2S,3S,4S(1S,2R,3R,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (36), (0.1 g), pmr (CDCl₃) (Figure V) δ 1.19 (d, J 7 Hz, 3, C(4)CH₃), δ 2.43 (s, $W_{\frac{h}{2}}$ 4 Hz, 1, C(1)OH), δ 2.47 (d of q, J 7.0 Hz, J' 2 Hz, 1, C(4)H), δ 3.70 (d, J 2 Hz, 1, C(3)H), δ 4.05 (d of d, J 2 Hz, J' 2 Hz, 1, C(2)H), δ 7.33 (m, $W_{\frac{h}{2}}$ 4 Hz, 5, C₆H₅); The chemical shift of the C(1)OH on extrapolation to infinite dilution

absorbed at $\xi 1.9$ (Figure VIII); ν_{\max} 3594 - 3454, 1500, 1453, 1185, 990, 937, 841 and 708 cm^{-1} ; $\lambda_{\max}^{\text{EtOH}}$ 246.3 nm ($\epsilon 598$), 251.5 ($\epsilon 587$), 257.5 ($\epsilon 530$), 264.0 ($\epsilon 413$).

Pmr spectra of 35 and 36 on addition of $\text{Eu}(\text{fod})_3$ to deuteriochloroform solutions are shown in Figures VI and VII respectively.

Photolysis of a mixture (1:15) of 2S,3S(2R,3R)- and 2S,3R(2R,3S)- 3,4-epoxy-2-methyl-1-phenyl-1-butanones (2) and (3) (0.06 g) enriched in the latter isomer, under the same conditions as above for 17 hours afforded 1R,2R,3R,4S(1S,2S,3S,4R)-2,3-epoxy-4-methyl-1-phenyl-1-cyclobutanol (35), (0.03 g), mp 84 - 5 $^{\circ}$, pmr (CDCl_3) $\delta 0.98$ (d, J 8 Hz, C(4)CH $_3$).

1-Bromo-3-methyl-2-butene

1-Bromo-3-methyl-2-butene was prepared⁶⁸ according to the literature procedure. 2-Methyl-1,3-butadiene (commercial grade, 100 g, 1.5 M) was cooled to ice temperature and was added to a solution of hydrogen bromide in glacial acetic acid (45% w/v HBr) (122 g, 1.5 M) and the mixture left standing at 0 $^{\circ}$ for 2 days. The reaction mixture was added to ice water (2000 cc) and stirred. On standing, a layer of oil separated. This oil was dried with anhydrous calcium chloride and distilled under reduced pressure (50 $^{\circ}$, 20 mm Hg) to give 1-bromo-3-methyl-2-butene (155 g), pmr (CCl_4)

$\delta 1.75$ (s, 3, C(3)CH₃), $\delta 1.78$ (s, 3, C(4)H₃), $\delta 3.98$ (d, J 8.5 Hz, 2, C(1)H₂), $\delta 5.52$ (t, J 8.5 Hz, 1, C(2)H).

2,2-Dimethyl-1-phenyl-3-buten-1-ol (20)

1-Bromo-3-methyl-2-butene (25 g, 0.66 M) in anhydrous ether (50 cc) was added dropwise over a period of 1 hour to a stirred solution of magnesium filings (8 g) in ether (100 cc) under nitrogen atmosphere at 0°. After the addition was complete, the reaction mixture was stirred for a further 3 hours. The solution was decanted into a clean round bottom flask previously flushed with dry nitrogen. Benzaldehyde (analytical grade, 9 g, 0.08 M) in ether (30 cc) was added slowly to the Grignard reagent and the resulting mixture was left stirring overnight at room temperature. A saturated solution of ammonium chloride was added dropwise. The ether layer and subsequent ether washings were dried with anhydrous magnesium sulphate and the solvent removed by distillation. The product was adsorbed on 5% deactivated alumina. Elution with petroleum ether gave 2,2-dimethyl-1-phenyl-3-buten-1-one (21)⁶⁹, (1.8 g), pmr (CDCl₃) $\delta 1.40$ (s, 6, C(2)CH₃'s), $\delta 5.20$ (m, $W_{\frac{h}{2}}$ 20 Hz, 2, C(4)H₂), $\delta 6.20$ (d of d, J 18 Hz, J' 10 Hz, 1, C(3)H), $\delta 7.35$ (m, 3, aromatic protons), $\delta 7.83$ (m, 2, aromatic protons); ν_{\max}^{film} 2981, 1681, 1638, 1603, 1581, 1470, 1449, 1248, 1167, 1153, 975, 923, 806, 727 and 708 cm⁻¹; $\lambda_{\max}^{\text{EtOH}}$ 243.7 nm ($\epsilon 9.2 \times 10^3$); mass spectrum M⁺ 174.1048 (calc. for

$C_{12}H_{14}O$, 174.1045). Further elution with petroleum ether - ether (10 : 2) gave 2,2-dimethyl-1-phenyl-3-buten-1-ol (20) (2.1 g), pmr⁶⁴ ($CDCl_3$) δ 0.95 (s, 3, C(2)CH₃), δ 1.00 (s, 3, C(2)CH₃), δ 2.13 (d, J 3.0 Hz, 1, OH), δ 4.37 (d, J 3 Hz, 1, C(1)H), δ 4.83 - 6.20 (m, 3, C(3)H and C(4)H₂), δ 7.27 (m, $W_{\frac{h}{2}}$ 3 Hz, 5, C₆H₅); ν_{\max}^{film} 3485, 2981, 1497, 1457, 1026, 916, 787, 737 and 711 cm^{-1} ; $\lambda_{\max}^{\text{EtOH}}$ 247.2 nm (ϵ 344), 252.0 (ϵ 358), 258.0 (ϵ 309), 264.4 (ϵ 211); mass spectrum M^+ 176.1202 (calc. for $C_{12}H_{16}O$, 176.1201). Elution with petroleum ether - ether (10 : 4) gave benzyl alcohol (1.5 g, 15%), pmr ($CDCl_3$) δ 2.87 (s, $W_{\frac{h}{2}}$ 10 Hz, 1, OH), δ 4.55 (s, $W_{\frac{h}{2}}$ 6 Hz, 2, methylene protons), δ 7.30 (m, 5, C₆H₅); ν_{\max}^{film} 3355, 1499, 1456, 1200, 1019, 743 and 705 cm^{-1} .

1R,3S(1S,3R)- and 1S,3S(1R,3R)- 3,4-Epoxy-2,2-dimethyl-1-phenyl-1-butanols (22) and (23)

To a solution of meta-chloroperbenzoic acid (3 g) in anhydrous ether (100 cc) was added 2,2-dimethyl-1-phenyl-3-buten-1-ol (20) (1.5 g). The reaction was kept at room temperature for a week. Solid potassium carbonate was added to neutralise the acid. The mixture was then filtered through an alumina column and solvent removed by distillation to give the crude product which was adsorbed onto 5% deactivated alumina. Elution with petroleum ether - ether (10 : 2) gave starting material (20) (0.15 g), pmr ($CDCl_3$) δ 0.95 and 1.00 (C(2)CH₃'s) and a mixture of 3,4-epoxy-2,2-di-

methyl-1-phenyl-1-butanols (22) and (23) (1.3 g),

$\nu_{\text{max}}^{\text{film}}$ 3455, 2980, 1495, 1475, 1455, 1405, 1045, 1020, 910, 865, 770, 733, 710 and 605 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 247.3 nm (ϵ 169), 252.1 (ϵ 199), 258.1 (ϵ 212), 264.2 (ϵ 152); mass spectrum M^+ 192.1142 (calc. for $\text{C}_{12}\text{H}_{16}\text{O}_2$, 192.1150); pmr (CDCl_3) δ 0.80 (s, C(2)CH₃'s), δ 0.83 and δ 0.75 (C(2)CH₃'s of the other isomer), δ 2.57 (m, $W_{\frac{h}{2}}$ 12 Hz, C(4)H₂), δ 2.88 (m, $W_{\frac{h}{2}}$ 14 Hz, C(3)H and OH), δ 4.48 (d, J 2 Hz, C(1)H), δ 4.55 (d, J 2 Hz, C(1)H of the other isomer), δ 7.30 (m, $W_{\frac{h}{2}}$ 3 Hz, C₆H₅).

3S(3R)-3,4-Epoxy-2,2-dimethyl-1-phenyl-1-butanone (4)

A mixture of chromium trioxide⁶⁰ (1.5 g) and anhydrous pyridine (2.38 g) was stirred in dichloromethane (40 cc) for 20 minutes. A solution of the 3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanols (22) and (23) (0.5 g) in dichloromethane (0.5 cc) was added and the mixture was stirred for a further 30 minutes. Isolation of the product in the usual manner afforded 3S(3R)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) (0.44 g), pmr (CDCl_3) δ 1.28 (s, 6, C(2)CH₃'s), δ 2.80 (m, 2, C(4)H₂), δ 3.20 (d of d, J 3 Hz, J' 4.5 Hz, 1, C(3)H), δ 7.43 (m, 3, aromatic) δ 7.87 (m, 2, aromatic); $\nu_{\text{max}}^{\text{film}}$ 2983, 2933, 1681, 1606, 1584, 1473, 1406, 1252, 1168, 971, 923, 886, 845, 726, 708 and 638 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 244.2 nm (ϵ 0.80 x 10⁴), 278.5 (ϵ 0.76 x 10³), 323.0 (ϵ 138); mass spectrum M^+ 190.0993 (calc. for $\text{C}_{12}\text{H}_{14}\text{O}_2$, 190.0994). This compound (4) is more

stable than 3,4-epoxy-1-phenyl-1-butanone (1) and can be stored at 0° for long periods.

Photolysis of 3S(3R)-3,4-epoxy-2,2-dimethyl-1-phenyl-1-butanone (4)

3S(3R)-3,4-Epoxy-2,2-dimethyl-1-phenyl-1-butanone (4) (0.55 g) dissolved in anhydrous benzene (300 cc) in a pyrex reaction vessel was degassed in the usual manner and photolysed using 3000 Å UV lamps⁷². After 4½ hours, three products (two major and one minor) could be detected by tlc on alumina. The least polar photoproduct (0.07 g) was stable to chromatography on deactivated alumina and was eluted with petroleum ether. Pure fractions of this product were obtained but subsequent column fractions were contaminated with starting material (4). Both compounds had identical retention on a tlc plate.

This photoproduct was identified as 3-methyl-2-buten-1-ol benzoate (29)⁷¹, pmr (CDCl₃) δ 1.78 (s, 6, C(4)H₃ and C(3)CH₃), δ 4.80 (d, J 7.0 Hz, 2, C(1)H₂), δ 5.47 (complex triplet, J 7.0 Hz, 1, C(2)H), δ 7.50 (m, 3, aromatic), δ 7.97 (m, 2, aromatic). Double irradiation experiments showed the doublet at δ 4.80 to be coupled with the triplet at δ 5.47. $\nu_{\text{max}}^{\text{film}}$ 3000, 1723, 1606, 1455, 1363, 1259, 1170, 1104, 1069, 1027, 938 and 720 cm⁻¹; $\lambda_{\text{max}}^{\text{EtOH}}$ 229.2 nm (ϵ 1.30 x 10⁴); mass spectrum M⁺ 190.0996 (calc. for C₁₂H₁₄O₂, 190.0994). The product was identical in all res-

pects with an authentic sample. Further elution with petroleum ether - ether (10 : 2) gave the minor component (0.01 g) which was recrystallised from methanol (mp 98 - 100°) and identified as 2,3-epoxy-4,4-dimethyl-1-phenyl-1-cyclobutanol (39), pmr (CDCl₃) (Figure IX) δ 0.60 (s, 3, C(4)CH₃), δ 1.00 (s, 3, C(4)CH₃), δ 2.68 (s, $W_{\frac{h}{2}}$ 6 Hz, 1, OH), δ 3.57 (d, J 2 Hz, 1, C(3)H), δ 4.17 (d, J 2 Hz, 1, C(2)H), δ 7.27 (m, $W_{\frac{h}{2}}$ 3 Hz, 5, C₆H₅); $\nu_{\text{max}}^{\text{CHCl}_3}$ 3575, 708 cm⁻¹.

Attempts to measure the parent ion in the mass spectrometer were not successful. The other major product was unstable on an alumina column and decomposed rapidly even at 0°. Repeated attempts to isolate this product or its decomposition product(s) were not successful. It was likely that this compound was a primary photoproduct since photolysis of 3-methyl-2-buten-1-ol benzoate (29) under similar conditions remained unchanged.

3-Methyl-2-buten-1-ol benzoate (29)⁷¹

A mixture of 1-bromo-3-methyl-2-butene (12 g) and sodium benzoate (9.6 g) in benzene (60 cc) was heated under reflux for 12 hours. Filtration of the reaction mixture and removal of the solvent by distillation (40°, 30 mm Hg) gave 3-methyl-2-buten-1-ol benzoate (29) which was purified by column chromatography on 5% deactivated alumina. Elution with petroleum ether gave pure 3-methyl-2-buten-1-ol benzoate (29)

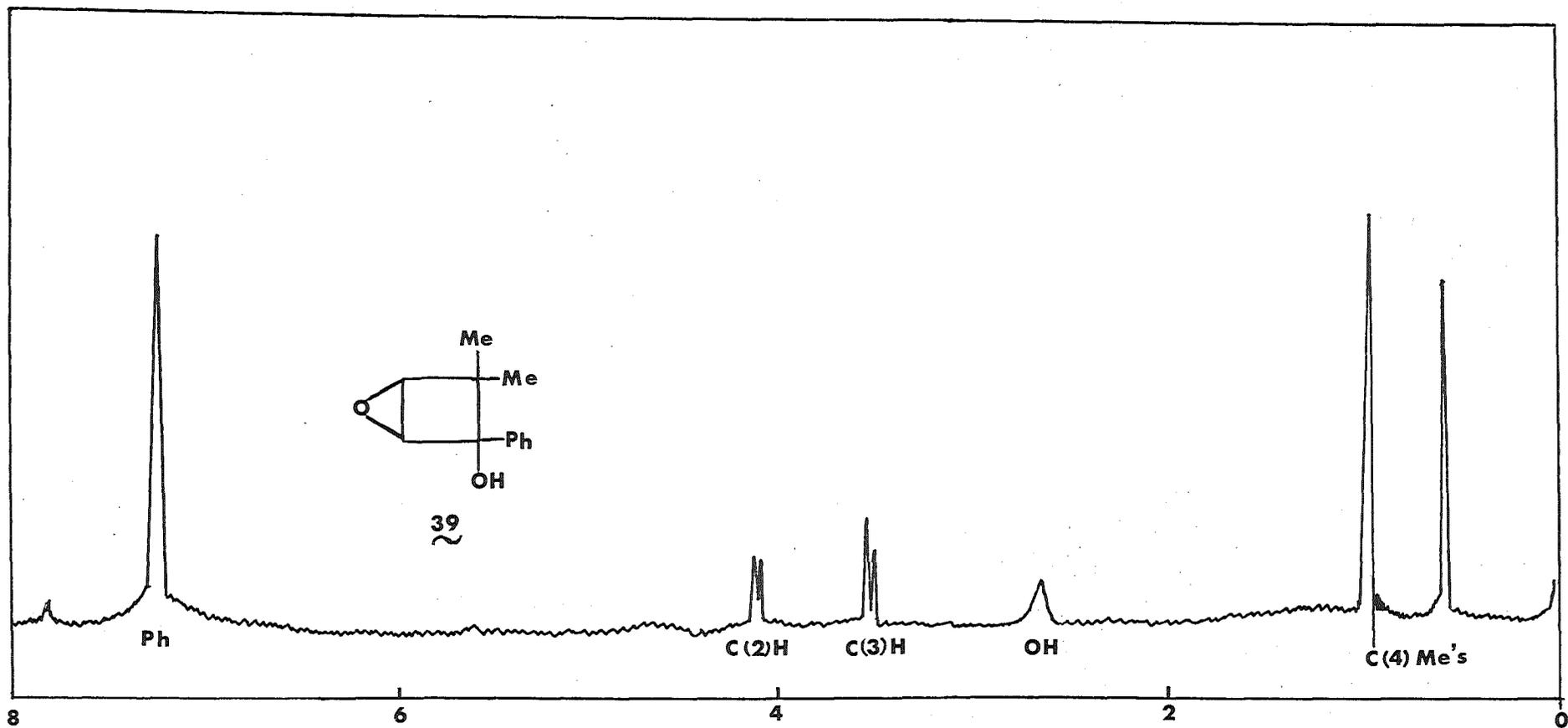


Figure IX ppm(δ) 60 MHz PMR

(2.6 g), pmr (CDCl_3) δ 1.78 (s, 6, $\text{C}(4)\text{H}_3$ and $\text{C}(3)\text{CH}_3$), δ 4.80 (d, J 7 Hz, 2, $\text{C}(1)\text{H}_2$), δ 5.47 (complex triplet, J 7 Hz, 1, $\text{C}(2)\text{H}$), δ 7.50 (m, 3, aromatic), δ 7.97 (m, 2, aromatic). $\nu_{\text{max}}^{\text{film}}$ 3000, 1723, 1606, 1455, 1363, 1259, 1170, 1104, 1069, 1027, 938 and 720 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 229.2 nm (ϵ 1.30×10^4).

Ethenyl acetate (26)

Ethenyl acetate (26) is commercially available from Koch-Light-Laboratories Ltd., Colnbrook, Bucks, England. Pmr (CDCl_3) δ 2.07 (s, 3, COCH_3), δ 4.57 (d of d, J 7 Hz, J' 1.5, 1, $\text{C}(2)\text{H}$ trans to acetate), δ 4.83 (d of d, J 14 Hz, J' 1.5 Hz, 1, $\text{C}(2)\text{H}$ cis to acetate), δ 7.30 (d of d, J 14 Hz, J' 7 Hz, 1, $\text{C}(1)\text{H}$); $\nu_{\text{max}}^{\text{film}}$ 1763, 1647, 1355, 1280, 1132, 1018, 953 and 878 cm^{-1} .

Ethenyl benzoate (27)

A mixture of ethenyl acetate (26) (34.5 g), benzoic acid (18.5 g), mercuric acetate (0.5 g) and sulphuric acid (conc) (0.05 cc) was heated under reflux on an oil bath until the temperature of the mixture reached 140° . The low boiling constituents (mostly ethenyl acetate (26)) were distilled off at atmospheric pressure to give a dense black residue.

Fractional distillation of this mixture at reduced pressure (90° , 15 mm Hg) gave the required ethenyl benzoate (27) and three other high boiling diester compounds. Ethenyl benzoate (27) was purified by redistillation (10 g), pmr (CDCl_3) δ 4.65 (d of d, J 7.0 Hz, J' 1.5 Hz, 1, C(2)H trans to benzoate), δ 5.03 (d of d, J 14 Hz, J' 1.5 Hz, 1, (C2)H cis to benzoate), δ 7.33 - 8.20 (m, 6, C_6H_5 and C(1)H); $\nu_{\text{max}}^{\text{film}}$ 1737, 1647, 1600, 1452, 1277, 1247, 1162, 1130, 1087, 1064, 1022, 947, 872, 715 and 702 cm^{-1} ; mass spectrum M^+ 148.0522 (calc. for $\text{C}_9\text{H}_8\text{O}_2$, 148.0524). Other prominent peaks are at 105 ($\text{C}_7\text{H}_5\text{O}^+$) and 77 (C_6H_5^+).

Oxiranyl benzoate (25)

Ethenyl benzoate (27) (1.0 g) was dissolved in dry methylene chloride (60 cc) and meta-chloroperbenzoic acid (2.6 g) was added. The reaction was allowed to stand at room temperature for 7 days. Potassium carbonate crystals were added and the resulting mixture stirred for 10 minutes. It was then rapidly filtered through a small column of alumina, assisted by suction. The column was further washed with two volumes of ether (2 x 30 cc). The combined ether and methylene chloride extracts were distilled at 40° under reduced pressure (20 mm Hg) to give oxiranyl benzoate (25) (0.9 g), pmr (CDCl_3)

δ 2.97 (m, $W_{\frac{h}{2}}$ 9 Hz, 2, C(2)H₂), δ 5.80 (d of d, J 2.5 Hz, J' 1.0 Hz, 1, C(1)H), δ 7.40 - 8.01 (m, 5, C₆H₅); ν_{\max}^{film} 1735, 1600, 1451, 1298, 1253, 1105, 1062, 1020, 950, 855 and 713 cm⁻¹; mass spectrum M⁺ 164.0470 (calc. for C₉H₈O₃, 164.0473). Other prominent peaks are at 105 (C₇H₅O)⁺ and 77 (C₆H₅)⁺.

Photolysis of oxiranyl benzoate (25)

The following solutions of oxiranyl benzoate (25) were photolysed in the usual manner :

1. 0.21 g in anhydrous benzene (100 cc, pyrex reaction vessel) was photolysed for 22 hours using 3000 Å UV lamps⁷².
2. 0.20 g in pentane (100 cc, quartz vessel) for 22 hours using 2537 Å lamps⁷².
3. 0.12 g in acetonitrile (100 cc, quartz vessel) for 22 hours using 2537 Å lamps.
4. 0.10 g in dichloromethane (100 cc, quartz vessel) for 20 hours using 2537 Å lamps.
5. 0.12 g in dichloromethane (100 cc, quartz) for 8 hours using 1849 - 2537 Å lamps⁷².

Photolysis was followed by pmr spectral

analysis. No reaction could be detected for solutions 1, 2, 3 and 4. However, the pmr spectrum of the photolysis solution 5 indicated the absence of starting material and showed the presence of new peaks. Removal of solvent by distillation gave 1-chloro-2-hydroxyethyl benzoate (46) (0.13 g), pmr (CDCl_3) δ 4.87 (s, $w_{\frac{h}{2}}$ 15 Hz, 1, OH), δ 4.05 (d, J 5.5 Hz, 2, C(2)H₂), δ 6.72 (t, J 5.5 Hz, 1, C(1)H), δ 7.34 - 8.20 (m, 5, C₆H₅); $\nu_{\text{max}}^{\text{film}}$ 3450, 1742, 1603, 1453, 1250, 1062 and 714 cm^{-1} .

Acetylation of 1-chloro-2-hydroxyethyl benzoate (46)

To a solution of 1-chloro-2-hydroxyethyl benzoate (46) (0.10 g) in chloroform (5 cc) was added N,N-dimethylaniline (0.20 g), and acetylchloride (0.14 g) and the mixture stirred at room temperature for 5½ hours. Dichloromethane (20 cc) was added to the reaction mixture and the solution washed with aqueous sulphuric acid (10 cc, 2½% by weight), saturated sodium bicarbonate (10 cc), water (5 x 15 cc), and dried with magnesium sulphate. Distillation under vacuum (30°, 20 mm Hg) gave a smelly dark coloured compound, 2-acetoxy-1-chloroethyl benzoate (47) (0.1 g), pmr (CDCl_3) δ 2.08 (s, 3, OCOCH₃), 4.56 (d, J 6 Hz, 2, C(2)H₂), δ 6.82 (t, J 6 Hz, 1, C(1)H), δ 7.43 - 8.22 (m, 5, C₆H₅); $\nu_{\text{max}}^{\text{film}}$ 1750, 1602, 1452, 1350, 1230, 1210, 1080, 1063 and 714 cm^{-1} ; Mass spectrum M⁺ 242.0337 (calc. for C₁₁H₁₁O₄Cl³⁵, 242.0346).

Reaction of oxiranyl benzoate (25) with p-toluene-
sulphonic acid

To a clean dry round bottom flask, sodium dried ether (125 cc) and oxiranyl benzoate (25) (0.10 g) were added. The mixture was stirred and p-toluenesulphonic acid (0.12 g) added. The reaction was allowed to proceed for $3\frac{1}{2}$ hours at room temperature and then quenched with saturated potassium carbonate (0.5 cc). After a further 15 minutes stirring, anhydrous potassium carbonate and anhydrous magnesium sulphate were added. The solid was removed by filtration and the ether by careful distillation (30° , 20 mm Hg) to give 2-hydroxy-1-tosyloxyethyl benzoate (48) (0.12 g), pmr (CDCl_3) δ 2.20 (s, 3, $\text{pC}_6\text{H}_4\text{-CH}_3$), δ 3.90 (d, J 4.5 Hz, 2, $\text{C}(2)\text{H}_2$), δ 3.28 (broad singlet, W_2^{h} 12 Hz, 1, OH), δ 6.88 (t, J 4.5 Hz, 1, $\text{C}(1)\text{H}$), δ 7.10 - 8.23 (m, 9, C_6H_5 and C_6H_4); $\nu_{\text{max}}^{\text{film}}$ 3520, 2845, 1735, 1597, 1450, 1355, 1253, 1183, 1171, 1064, 895, 817, 715, 578 and 566 cm^{-1} . 2-Hydroxy-1-tosyloxyethyl benzoate (48) decomposed in the mass spectrometer so that no parent ion was detected.

On standing overnight at room temperature, 2-hydroxy-1-tosyloxyethyl benzoate (48) decomposed into two solid products, both soluble in water. The compounds were separated by preferential dissolution of one product into chloroform. The

chloroform extract, after removal of solvent and subsequent recrystallisation from water gave benzoic acid (mp 116 - 119° cf. lit. value 126°); mass spectrum M^+ 122.0368 (calc. for $C_7H_6O_2$, 122.0368). The pmr spectrum was identical to that of an authentic sample. The insoluble product was identified as p-toluenesulphonic acid, pmr (CD_3CN) δ 2.40 (s, $C_6H_4-CH_3$), δ 7.37 (d, J 8 Hz) and δ 7.77 (d, J 8 Hz) (aromatics) and was consistent with the pmr spectrum of an authentic sample (δ 2.40 (s), δ 7.37 (J 8 Hz), and δ 7.77 (J 8 Hz)).

In a repeat experiment, when the oxiranyl benzoate (25) was reacted with a catalytic amount of p-toluenesulphonic acid, only a small amount of 2-hydroxy-1-tosyloxyethyl benzoate (49) could be detected after $3\frac{1}{2}$ hours. The reaction mixture was largely starting material. After 12 hours no trace of starting material could be detected and recrystallisation from water gave benzoic acid crystals.

Acetylation of 2-hydroxy-1-tosyloxyethyl benzoate (48)

To a solution of freshly prepared 2-hydroxy-1-tosyloxyethyl benzoate (48) (0.1 g) in chloroform (5 cc) was added N,N-dimethylaniline (0.2 g) and acetylchloride (0.14 g) and the solution stirred at

room temperature for $5\frac{1}{2}$ hours. The reaction mixture was then added to dichloromethane (20 cc), washed with aqueous sulphuric acid (10 cc, 2 $\frac{1}{2}$ % by weight), saturated sodium bicarbonate (10 cc), water (5 x 15 cc), dried with magnesium sulphate and distilled under vacuum (40° , 20 mm Hg) to give 2-acetoxy-1-tosyloxyethyl benzoate, pmr (CDCl_3) δ 2.08 (s, 3, $-\text{OCOCH}_3$), δ 3.28 (s, 3, $p\text{-C}_6\text{H}_4\text{-CH}_3$), δ 4.58 (d, J 5.0 Hz, C(2)H₂), 6.85 (t, J 5.0 Hz, C(1)H), δ 7.07 - 8.40 (m, 9, C_6H_5 and C_6H_4). Double irradiation experiments indicated that the doublet at δ 4.58 was coupled to the triplet centred at δ 6.85.

2,3-Epoxy-3-methyl-1-butanol benzoate (28)

To a solution of 3-methyl-2-buten-1-ol benzoate (29) (0.5 g) in ether (50 cc) was added meta-chloroperbenzoic acid (1.0 g) and ether (50 cc). The reaction was heated under reflux for $2\frac{1}{2}$ hours. The reaction was quenched by the addition of excess anhydrous potassium carbonate. The solid was removed by filtration and the ether removed by vacuum distillation. The crude product was adsorbed onto 5% deactivated alumina and elution with petroleum ether - ether (10 : 2) gave 2,3-epoxy-3-methyl-1-butanol benzoate (28), pmr (CDCl_3), δ 1.38 (s, 6, C(4)H₃ and C(3)CH₃), δ 3.13 (d of d, J 4.5 Hz, J' 6.5 Hz, 1, C(2)H), δ 4.34 (d of d, J 12.5 Hz, J' 6.5 Hz, 1, C(1)H), δ 4.60 (d of d, J

12.5 Hz, J' 4.5 Hz, 1, C(1)H, δ 7.40 - 8.23 (m, 5, C₆H₅). (By double irradiation experiments it was shown that C(1)H₂ and C(2)H were coupled. Irradiation at δ 3.13 reduced the methylene cluster to a A,B quartet); $\nu_{\text{max}}^{\text{film}}$ 2978, 1723, 1604, 1455, 1362, 1303, 1261, 1170, 1109, 1069, 1025 and 720 cm⁻¹.

Photolysis of 2,3-epoxy-3-methyl-1-butanol benzoate (28)

The following solutions of 2,3-epoxy-3-methyl-1-butanol benzoate (28) were prepared and the photolysis experiments carried out;

1. 0.04 g in anhydrous benzene (40 cc, pyrex container) was photolysed for 16 hours, using 3000 Å UV lamps.⁷²
2. 0.05 g, in benzene (50 cc, quartz vessel) was photolysed for 7½ hours, using 2537 Å lamps.⁷²
3. 0.05 g, in anhydrous pentane (50 cc) was photolysed for 15 hours, using 1849 - 2537 Å lamps.⁷²

In all these reactions, 2,3-epoxy-3-methyl-1-butanol benzoate (28) remained unchanged.

4,5-Epoxy-2-pentanol

Epoxidation of 4-penten-2-ol (Aldrich), pmr (CDCl₃) δ 1.17 (d, J 6.5 Hz, 3, C(1)H₃), δ 2.23 (t,

J 6 Hz, 2, C(3)H₂), δ 2.57 (s, $W_{\frac{h}{2}}$ 2 Hz, 1, OH), δ 3.83 (m, $W_{\frac{h}{2}}$ 32 Hz, 1, C(2)H), δ 4.87 - 6.23 (m, 3, C(4)H and C(5)H₂), with meta-chloroperbenzoic acid in ether at 0° for 3 weeks gave 4,5-epoxy-2-pentanol, purified by preparative gas chromatography on SE 30, 10% on 30/60 mesh chromosorb W, in a 4.8 m x 0.3 cm² copper column, pmr (CDCl₃) δ 1.25 (d, J 6.5 Hz, 3, C(1)H₃), δ 1.73 (m, $W_{\frac{h}{2}}$ 34 Hz, 2, C(3)H₂), δ 2.40 (broad singlet, $W_{\frac{h}{2}}$ 7 Hz, 1, OH), δ 2.40 - 3.30 (m, 3, C(4)H and C(5)H₂), δ 4.07 (m, 1, C(2)H); ν_{\max}^{film} 3410, 2970, 1363, 1253, 1133, 1097, 960, 926, 860 and 836 cm⁻¹.

4,5-Epoxy-2-pentanone (24)

Repeated attempts to oxidise 4,5-epoxy-2-pentanol by chromium trioxide-pyridine complex in anhydrous dichloromethane led to decomposition of starting material. Under the alternative oxidising conditions - MnO₂ in CH₂Cl₂, C₆H₅CN-H₂O₂, RuO₂-NaIO₄ - only starting material could be isolated.

4-Penten-2-one

A solution of organo-magnesium Grignard prepared from 1-bromo-2-propene (24 g) in ether at dry ice-acetone temperature was added slowly (1 hour) to a stirred solution of acetic anhydride (41 g) in dry ether (100 cc) at -78°. After vigorous stirring for 2 - 3 hours, the cooling bath was removed and the mixture was treated with ammonium chloride solution,

washed with water, dried over magnesium and ether distilled off to give a mixture of two products which on fractional distillation (40°, 30 mm Hg) gave 4-penten-2-one (1.5 g), pmr (CDCl₃) δ 2.01 (s, 3, C(1)H₃) δ 4.63 (d, J 5 Hz, 2, C(3)H₂), δ 5.13 - 6.40 (m, 3, C(4)H and C(5)H₂); $\nu_{\text{max}}^{\text{film}}$ 2900, 1743, 1396 and 1357 cm⁻¹ and 4-methyl-1,6-heptadien-4-ol (5.4 g), pmr (CDCl₃) δ 1.18 (s, 1, C(4)CH₃), δ 1.82 (s, 1, OH, addition of D₂O resulted in the disappearance of this peak), δ 2.28 (d, J 7 Hz, 4, C(3)H₂ and C(5)H₂), δ 4.92 - 6.38 (m, 6, C(1)H₂, C(2)H, C(6)H and C(7)H₂); $\nu_{\text{max}}^{\text{film}}$ 3430, 3180, 2980, 1644 and 1362 cm⁻¹; mass spectrum M⁺ 216 (calc. for C₈H₁₄O, 216).

4,5-Epoxy-2-pentanone (24)

Attempts to epoxidise 4-penten-2-one with meta-chloroperbenzoic acid or monoperoxyphthalic acid in ether at room temperature were unsuccessful.

APPENDIX I

4 α ,5-Epoxy-5 α -cholest-2-ene (51)

4 α ,5-Epoxy-5 α -cholest-2-ene (51) was prepared⁸² by the solvolysis of 4 α ,5-epoxy-3 α -tosyloxy-5 α -cholestane in collidine, mp 87 - 8° , pmr (CDCl₃)

$\delta 0.70$ (C(18)H₃), $\delta 0.82$, $\delta 0.93$ (side chain methyls),
 $\delta 0.93$ (C(19)H₃), $\delta 3.01$ (d of d, J 2.5 Hz, J' 2.5 Hz,
 C(4)H, collapsed to a singlet, by double irradiation
 at $\delta 5.86$), $\delta 5.86$ (d, J 2.5 Hz, C(2)H and C(3)H,
 collapsed to a singlet, $W_{\frac{h}{2}}$ 3.5 Hz on double irradiat-
 ion at $\delta 3.01$); ν_{\max} 3060, 1646, 959, 934, 921,
 894, 788, 777, 718 and 679 cm⁻¹; λ_{\max} 212.0 nm (ϵ
 4.2×10^3); (found : C, 84.5; H, 11.9; C₂₇H₄₄O requires
 C, 84.4; H, 11.5%).

Photolysis of 4 α ,5-epoxy-5 α -cholest-2-ene (51)

In a typical experiment, a solution of 4 α ,5-
 epoxy-5 α -cholest-2-ene (51) (0.18 g) in dry degassed
 acetone (100 cc) in an atmosphere of nitrogen was
 photolysed with 3000 Å UV lamps for 10 hours. After
 removal of solvent, the residue was adsorbed onto 5%
 deactivated alumina (20 g). Elution with petroleum
 ether - ether (100 : 2) gave a trace of starting mat-
 erial (0.01 g) and A-nor-B-homo-5 β -cholest-2-en-6-one
 (53) (0.11 g) crystallised as plates from methanol,
 mp 83 - 4°; ν_{\max} 2950, 1709, 1469, 1361 and 699 cm⁻¹;
 $\lambda_{\max}^{\text{MeOH}}$ 230 nm ($\epsilon 20$), 240 ($\epsilon 20$); pmr (CDCl₃) δ 0.72
 (s, 3, C(18)H₃), δ 0.82 and 0.90 (side chain CH₃'s), 1.15 (s, 3,
 C(19)H₃), δ 3.58 (s, $W_{\frac{h}{2}}$ 6 Hz, 1, C(5)H), δ 5.55 ($W_{\frac{h}{2}}$
 8 Hz, 1, C(2)H), δ 5.90 ($W_{\frac{h}{2}}$ 8 Hz, 1, C(3)H). Double
 irradiation on any of the last three peaks led to
 sharpening of the other two; O.R.D. (in ethanol)

Φ_{350} -1954, Φ_{335} -2490, Φ_{325} -3352,

Φ_{315} -4501,	Φ_{307} -5364	Φ_{300} -4884,
Φ_{290} -2298,	Φ_{281} 0,	Φ_{278} + 575,
Φ_{275} +1053,	Φ_{269} +1244,	Φ_{265} +1149,
Φ_{260} + 575,	Φ_{256} 0 ;	mass spectrum M^+

384.3403 (calc. for $C_{27}H_{44}O$, 384.3392), (found C, 84.3 ; H, 11.5 , requires C, 84.4 ; H, 11.5 %).

Hydrogenation of A-nor-B-homo-5 β -cholest-2-en-6-one (53)

A-Nor-B-homo-5 β -cholest-2-en-6-one (53) (0.03 g), palladium on carbon (5%, 0.02 g) and pentane (25 cc) were placed in a round bottom flask and fitted to a low pressure hydrogenation apparatus and agitated for 3 $\frac{1}{2}$ hours in an atmosphere of hydrogen. The reaction mixture was then filtered to remove the catalyst and the solvent removed to give a crystalline product.

Recrystallisation from methanol gave colourless needles identified as A-nor-B-homo-5 β -cholestan-6-one (54) (0.02 g), mp 93 - 4 $^{\circ}$; ν_{max} 2956, 1709, 1368 cm^{-1} ; pmr ($CDCl_3$) δ 0.70 (s, 3, C(18)H₃), δ 0.82 and 0.90 (side chain CH₃'s), δ 1.07 (s, 3, C(19)H₃), δ 3.02 (d of d, J 8 Hz, J' 5 Hz, 1, C(5)H); O.R.D. (in ethanol)

Φ_{350} -1055,	Φ_{340} -1266,	Φ_{330} -1477,
Φ_{320} -2215,	Φ_{310} -3165,	Φ_{303} -3480,
Φ_{300} -3375,	Φ_{290} -1582,	Φ_{284} 0,
Φ_{280} +1371,	Φ_{270} +3271,	Φ_{260} +4325,

$\Phi_{255} +4429$, $\Phi_{250} +4320$; mass spectrum M^+
 386.3544 (calc. for $C_{27}H_{46}O$, 386.3548); (lit. value,⁸³
 ν_{\max} 1705 cm^{-1} ; O.R.D. a -63, λ_0 290).

Lithium aluminium hydride reduction of A-nor-B-homo-
 5 β -cholest-2-en-6-one (53)

Lithium aluminium hydride (0.03 g) was added to a solution of A-nor-B-homo-5 β -cholest-2-en-6-one (53) (0.02 g) in ether (10 cc). After stirring at room temperature for 5 hours, a solution of sodium sulphate was carefully added. The ether layer was separated from the sludge which was washed with more ether. The combined organic phases were washed with water and dried over anhydrous magnesium sulphate. The solvent was removed by distillation under reduced pressure and the residue adsorbed onto 5% de-activated alumina. Elution with petroleum ether - ether (10 : 6) gave A-nor-B-homo-5 β -cholest-2-en-6 α -ol (0.02 g), ν_{\max} 3423, 2943, 1463, 1383 cm^{-1} ; pmr ($CDCl_3$) δ 0.70 (s, 3, C(18)H₃), δ 0.95 (s, 3, C(19)H₃), δ 2.47 (s, 1, C(5 β)H), δ 4.00 (complex doublet, J 10 Hz, C(6 β)H), δ 5.45 and 5.84 (m, C(2)H and C(3)H).

4 β ,5-Epoxy-5 β -cholest-2-ene (52)

4 β ,5-Epoxy-5 β -cholest-2-ene (52) was obtained⁸² (in 24%) from treatment of 4 β ,5-epoxy-3 β -tosyloxy-5 β -

cholestane by heating under reflux in DMF containing LiCO_3 . Pmr (CDCl_3) δ 0.68 (s, 3, $\text{C}(18)\text{H}_3$), δ 0.82 and δ 0.92 (side chain CH_3 's), δ 1.09 (s, 3, $\text{C}(19)\text{H}_3$), δ 2.98 (d of d, J 2.5 Hz, J' 3.5 Hz, $\text{C}(4)\text{H}$, collapsed to a singlet by double irradiation at δ 5.83), δ 5.83 (m, $\frac{h}{2}$ 6 Hz, 2, $\text{C}(2)\text{H}$ and $\text{C}(3)\text{H}$).

Photolysis of 4 β ,5-epoxy-5 β -cholest-2-ene (52)

A solution of 4 β ,5-epoxy-5 β -cholest-2-ene (52) (0.14 g) in dry acetone (100 cc) was photolysed with 3000 Å ultraviolet lamps for 12 hours. The solvent was removed by distillation and tlc (silica, benzene) of the reaction mixture indicated two spots along with polar material.

Rapid column chromatography on 5% deactivated alumina gave, in the first few fractions, starting material (52) (0.02 g). Subsequent fractions contained A-nor-B-5 α -cholest-2-en-6-one (55) (0.04 g) as a relatively unstable oil, $\nu_{\text{max}}^{\text{film}}$ 2945, 1709, 1470, 1364 and 1164 cm^{-1} ; pmr (CDCl_3) δ 0.71 (s, 3, $\text{C}(18)\text{H}_3$), δ 0.82 (s, 3, $\text{C}(19)\text{H}_3$), δ 0.82 and 0.90 (side chain CH_3 's), δ 3.88 (m, $\frac{h}{2}$ 6 Hz, 1, $\text{C}(5)\text{H}$), δ 5.80 (m, $\frac{h}{2}$ 2 Hz, 2, $\text{C}(2)\text{H}$ and $\text{C}(3)\text{H}$); mass spectrum M^+ 384 (calculated for $\text{C}_{27}\text{H}_{44}\text{O}$, requires 384).

Hydrogenation of A-nor-B-homo-5 α -cholest-2-en-6-one (55)

A mixture of A-nor-B-homo-5 α -cholest-2-en-6-one (55) (0.03 g), palladium on carbon (5%, 0.03 g)

and pentane (30 cc) in an atmosphere of hydrogen was stirred for 9 hours. The reaction mixture was then filtered to remove the catalyst and the solvent removed by distillation to give a quantitative yield of A-nor-B-homo-5 α -cholestan-6-one (56). $\nu_{\text{max}}^{\text{film}}$ 2970, 1704, 1465 and 1359 cm^{-1} ; pmr (CDCl_3) δ 0.67 (s, 3, C(18)H₃), δ 0.67 (s, 3, C(19)H₃), 0.82 and 0.92 (side chain CH₃'s), δ 2.97 (m, $W_{\frac{h}{2}}$ 15 Hz, 1, C(5)H); O.R.D. (in ethanol).

Φ_{350} +1930,	Φ_{340} +2122,	Φ_{330} +2894,
Φ_{320} +3860,	Φ_{311} +4631,	Φ_{305} +3860,
Φ_{295} +1736,	Φ_{288} 0.	Φ_{280} -1351,
Φ_{275} -1925,	Φ_{270} -1930,	Φ_{265} -1544,

Φ_{260} -1351; mass spectrum M^+ 386.3551 (calc. for $\text{C}_{27}\text{H}_{46}\text{O}$, 386.3548) and by comparison with literature data⁸³; λ_{max} 1703 cm^{-1} ; δ 0.67 (C(18)H₃), δ 0.67 (C(10)H₃); a +136, λ_0 293 nm.

Equilibration of A-nor-B-homo-5 β -cholestan-6-one (54)

A mixture of A-nor-B-homo-5 β -cholestan-6-one (54) (0.05 g) and aqueous sulphuric acid (0.1 cc, 20%) in dioxane (5 cc) was refluxed in a nitrogen atmosphere at 100^o for 2 hours. The product was then extracted with ether and after removal of solvent gave an equilibrium mixture of isomeric A-nor-B-homo-5 β - and 5 α -cholestan-6-ones (54) and (56), pmr (CDCl_3) δ 0.67

(C(18)H₃ and C(19)H₃; 5 α -ketone), δ 0.70 and 1.07

(C(18)H₃ and C(19)H₃ respectively; 5 β -ketone),

O.R.D.	Φ_{350} +1425,	Φ_{340} +1730,	Φ_{330} +2341,
	Φ_{320} +3461,	Φ_{310} +4174,	Φ_{300} +2850,
	Φ_{290} 0.	Φ_{285} -1119,	Φ_{280} -2087,
	$\Phi_{269.5}$ -2810,	Φ_{265} -2545,	Φ_{255} -1934.

mass spectrum, M⁺ 386.3544 (calc. for C₂₇H₄₆O ,
386.3548 (Lit. value,⁸³ O.R.D. a + 88°).

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