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Photolysis of Some β,γ-Epoxycarbonyl Compounds

James M. Coxon and Gregory S. C. Hii

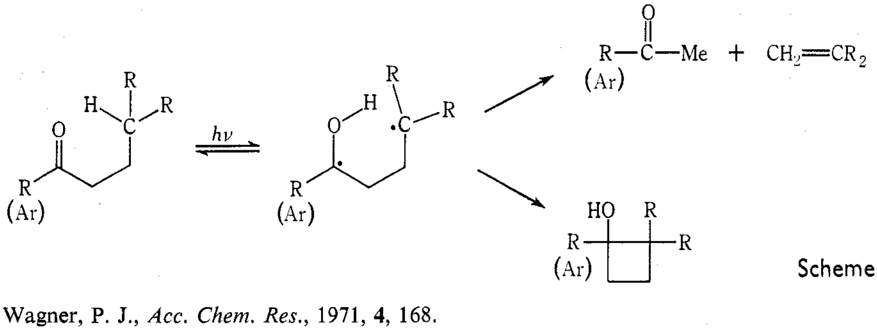
Department of Chemistry, University of Canterbury,
Christchurch, New Zealand.

Abstract

Photolysis of (3*RS*)-3,4-epoxy-1-phenylbutan-1-one (1a) gives in high yield a 1·7 : 1 mixture of (1*RS*,2*RS*,3*RS*)- and (1*RS*,2*SR*,3*SR*)-2,3-epoxy-1-phenylcyclobutan-1-ols (4) and (5). Fragmentation of the intermediate biradical is not a competitive reaction process. Alkyl substitution at C 2 facilitates α-cleavage while the 2-oxa analogue, oxiranyl benzoate (2), is unreactive under normal photolysis conditions.

Introduction

On photolysis alkyl and aryl butyl ketones,[1] which contain a C(γ)–H bond, undergo 1,5-hydrogen shifts to give biradical intermediates which react to give cyclization or fragmentation products (Scheme 1). Reactions of this type are known as Norrish type II photo-processes and are also observed for α-acetoxyacetophenones[2] and small ring α-cycloalkoxyacetophenones.[3] The photochemical reactions of β,γ-unsaturated ketones have received considerable attention[4] and a diverse range of products including cyclobutanols have been observed. Only scattered reports have appeared concerning the photochemistry of β,γ-epoxy ketones[5–10] and the only



Scheme 1

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[1] Wagner, P. J., *Acc. Chem. Res.*, 1971, **4**, 168.
[2] Lewis, F. D., and Turro, N. J., *J. Am. Chem. Soc.*, 1970, **92**, 311.
[3] Darling, T. R., Turro, N. J., Hirsch, R. H., and Lewis, F. D., *J. Am. Chem. Soc.*, 1974, **96**, 434.
[4] Houk, K. N., *Chem. Rev.*, 1976, 1.
[5] Starr, J. E., and Eastman, R. H., *J. Org. Chem.*, 1966, **31**, 1393.
[6] Chambers, R. J., and Marples, B. A., *J. Chem. Soc., Chem. Commun.*, 1972, 1122.
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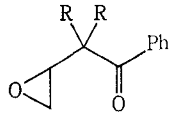
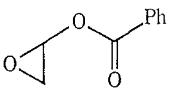
[8] Murray, R. K., Morgan, T. K., Hart, H., and Hull, V. J., *J. Org. Chem.*, 1973, **38**, 3805.
[9] Murray, R. K., and Goff, D. L., *J. Chem. Soc., Chem. Commun.*, 1973, 881.
[10] Murray, R. K., Morgan, T. K., Polley, J. A. S., Andruskiewicz, C. A., and Goff, D. L., *J. Am. Chem. Soc.*, 1975, **97**, 938.

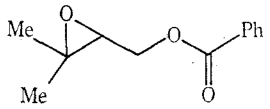
account of photolysis of acyclic β,γ-epoxy ketones is by Padwa *et al.*[11] who reported that *trans*-3,4-epoxy-1,4-diphenylbutan-1-one affords Norrish type II products. The *cis*-isomer was unreactive. We now report studies on the photolysis of 3,4-epoxy-1-phenylbutan-1-one (1a), the C2-dimethyl derivative, 3,4-epoxy-2,2-dimethyl-1-phenylbutan-1-one (1b), the 2-oxa analogue, oxiranyl benzoate (2), and 2,3-epoxy-3-methylbutyl benzoate (3).



(1a) R = H
(1b) R = Me



(2)



(3)

Discussion

3,4-Epoxy-1-phenylbutan-1-one (1a) was prepared by reaction of prop-2-enylmagnesium bromide with benzaldehyde[12] to give 1-phenylbut-3-en-1-ol which was oxidized with *m*-chloroperbenzoic acid to give a mixture of the isomeric 3,4-epoxy-1-phenylbutan-1-ols. Oxidation of these epoxy alcohols with chromium trioxide–pyridine complex[13] in anhydrous dichloromethane gave the required epoxy ketone (1a). The identity of this compound follows from the infrared, ultraviolet and p.m.r. spectrum. The epoxide (1a) is unstable and slowly decomposes to 4-hydroxy-1-phenylbut-2-en-1-one. The infrared (ν_{max} 1672 cm^{-1}) and ultraviolet (λ_{max} 257 nm, ε 22000) spectrum established the presence of the conjugated chromophore. The p.m.r. spectrum showed two olefinic protons (δ 7·20) and $C4\text{–}H_2$ centred at δ 4·50, the latter protons being deshielded by the hydroxyl and alkene groups. An attempt was made to determine the stereochemistry at the double bond by the addition of $Eu(fod)_3$ but this was not effective in differentiating the C2–H and C3–H due to peak broadening. Reaction of 4-hydroxy-1-phenylbut-2-en-1-one with a trace of hydrochloric acid in methanol gave 2-phenylfuran. Attempts to purify epoxide (1a) by distillation under reduced pressure failed, due to decomposition to give 2-phenylfuran, and so the crude reaction product obtained from epoxidation and oxidation was used directly in the photolysis experiments. 3,4-Epoxy-2,2-dimethyl-1-phenylbutan-1-one (1b) was prepared by reaction of the organomagnesium derivative of 1-bromo-3-methylbut-2-ene with benzaldehyde followed by epoxidation and oxidation of the alcohol. 2,2-Dimethyl-1-phenylbut-3-en-1-ol[14] was identified from the infrared and p.m.r. spectrum. In addition to 2,2-dimethyl-1-phenylbut-3-en-1-ol, 2,2-dimethyl-1-phenylbut-3-en-1-one and benzyl alcohol were isolated from the Grignard reaction. The identity of 2,2-dimethyl-1-phenylbut-3-en-1-one follows from the infrared (ν_{max} 1681 cm^{-1}), ultraviolet (λ_{max} 244 nm, ε 9200) and p.m.r. spectra which showed C3–H centred at δ 5·20 and coupled (*J* 10 Hz and 18 Hz) to the C4 protons. Epoxidation of 2,2-dimethyl-1-phenylbut-3-en-1-ol with *m*-chloroperbenzoic acid gave a mixture of the isomeric 3,4-epoxy-2,2-dimethyl-1-phenylbutan-

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[11] Padwa, A., Crumrine, D., Hartman, R., and Layton, R., *J. Am. Chem. Soc.*, 1967, **89**, 4435.

[12] Smith, G. G., and Voorhees, K. J., *J. Org. Chem.*, 1970, **35**, 2182.

[13] Ratcliffe, R., and Rodehorst, R., *J. Org. Chem.*, 1970, **35**, 4000.

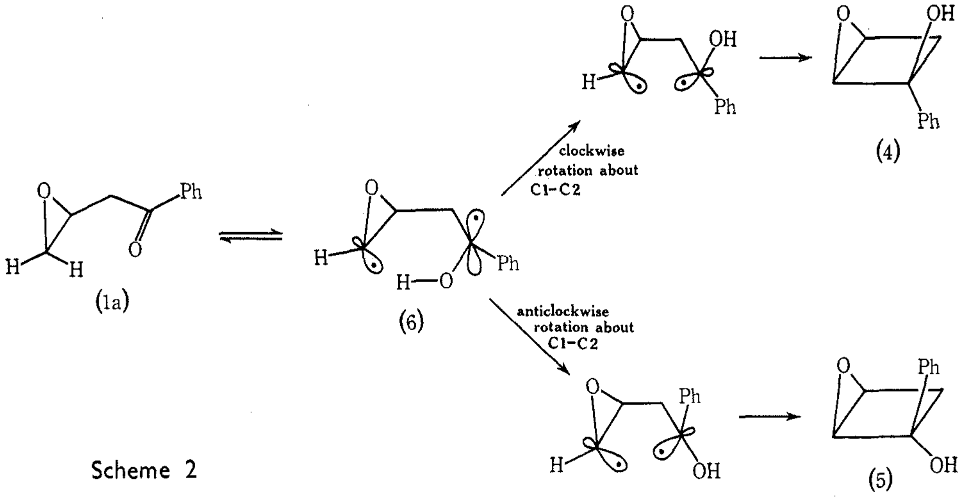
[14] Rautenstrauch, V., *Helv. Chim. Acta*, 1974, **57**, 496.

1-ols which was not separated but oxidized with chromium trioxide–pyridine complex[13] to 3,4-epoxy-2,2-dimethyl-1-phenylbutan-1-one. The p.m.r. spectrum of this compound showed C 3–H coupled with the C 4 protons (J 3 Hz and J 4·5 Hz) and the infrared and ultraviolet spectra showed the presence of the conjugated ketone chromophore. 2,3-Epoxy-3-methylbutyl benzoate (3) was prepared by epoxidation of 3-methylbut-2-enyl benzoate formed by reaction of 1-bromo-3-methylbut-2-ene with sodium benzoate. The p.m.r. spectrum of the epoxide showed C 2–H coupled (J 6·5 Hz and 4·5 Hz) to the C 1 protons which appeared as an AB quartet (J 12·5 Hz) with each proton further coupled with C 2–H. Oxiranyl benzoate (2) was prepared from ethenyl benzoate by reaction with *m*-chloroperbenzoic acid. C 1–H was coupled (J 2·5 Hz and 1·0 Hz) with C 2–H_2 and the infrared spectrum confirmed the presence of the ester chromophore.

Photolysis of (3*RS*)-3,4-epoxy-1-phenylbutan-1-one (1a) in benzene with 3000 Å lamps gave a reaction product mixture from which (1*RS*,2*RS*,3*RS*)-2,3-epoxy-1-phenylcyclobutan-1-ol (4) and (1*RS*,2*SR*,3*SR*)-2,3-epoxy-1-phenylcyclobutan-1-ol (5) (see Scheme 2 below) were isolated in 47 and 28% yield, respectively. The crude reaction product was examined by p.m.r. and g.l.c. in an attempt to detect acetophenone. The p.m.r. spectrum showed no absorption due to the methyl group of acetophenone but g.l.c. on both Carbowax 20M and SE 30 revealed a trace component (*c*. 2%) having the same retention time as acetophenone.

The identity of the cyclobutanols (4) and (5) follows from their mass spectra which show them to be isomeric with the starting epoxide and from infrared and detailed p.m.r. studies. The infrared spectra showed absorptions due to hydroxyl at 3600 and 3530 cm^{-1} for compound (4) and at 3620 and 3475 cm^{-1} for compound (5). The absorptions due to hydrogen-bonded hydroxyl were not apparent when the spectra were recorded for very dilute solutions. The p.m.r. spectra of the epoxycyclobutanols differed greatly in apparent complexity due to the chance identity of chemical shifts for C 2–H and C 3–H (δ 3·90) and C 4–H_2 (δ 2·27) for epoxide (5). This identity of the chemical shifts was removed by the addition of $Eu(fod)_3$ when the similarity between the isomers became apparent. In the p.m.r. spectrum, C 2–H and C 3–H for compound (4) appeared as an AB quartet (δ 3·99, H 2; δ 3·95, H 3; J 2 Hz) with C 2–H further coupled to C 4–H which is *syn* to the hydroxyl. The C 4 protons appeared as an AB quartet (δ 2·02, 2·50; J 12·5 Hz) with the upfield proton on the same face of the molecule as the hydroxyl, also coupled to C 2–H (J 2 Hz). The assignment of these protons was made possible by the addition of varying quantities of $Eu(fod)_3$; the C 4 proton *syn* to the hydroxyl, C 2–H and C 3–H, then moved more rapidly downfield than the other C 4 proton. C 2–H was more deshielded than C 3–H on addition of shift reagent due to the proximate effect of the hydroxyl group.

On addition of $Eu(fod)_3$ to epoxycyclobutanol (5), C 2–H and C 4–H *syn* to the hydroxyl moved more rapidly downfield than C 3–H and the other C 4 proton respectively. The epoxide protons were coupled (J 2 Hz) and the methylene protons appeared as an AB quartet with the downfield proton also coupled with C 2–H (J 2 Hz). The C 4 proton which is *syn* to both oxygen groups in isomer (4) moves more rapidly downfield on addition of shift reagent than either of the C 4 protons in epoxycyclobutanol (5) while the aromatic protons of the latter isomer are more sensitive to shift reagent than those of compound (4). This is consistent with the proximity of the phenyl to the epoxide group in isomer (5). The configuration of the isomers was further established from the concentration dependence of the chemical shift of the hydroxyl protons and their values when extrapolated to infinite dilution. For a compound exhibiting strong intramolecular hydrogen bonding only a small change in the chemical shift would be expected with change of concentration.[15] The concentration dependence of the chemical shift of the hydroxyl proton for isomer (5) was about twice that for isomer (4). The chemical shift of the hydroxyl proton on extrapolation to infinite dilution was δ 1·7 for isomer (5) and δ 2·7 for isomer (4). These values are consistent with the structural assignments.



Scheme 2

The epoxycyclobutanols (4) and (5) are envisaged to arise by excitation of the carbonyl and abstraction, by the carbonyl oxygen, of the γ-proton which is on the same face of the oxiran ring (Scheme 2). The 1,4-biradical species (6) is formed in a conformation where the radical orbitals are orthogonal and rotation about the C1–C2 bond can occur in a clockwise or an anticlockwise direction. The preference (*c.* 1·7 : 1·0) for formation of isomer (4), cf. (5), is thought to result from the steric compression between the epoxide oxygen and phenyl being greater than between the epoxide oxygen and hydroxyl. This steric interaction will be small until the 1,4-bond is well developed and the groups are close.

It is notable that fragmentation of the 1,4-biradical to give acetophenone and oxirene, a molecule which would only be stable at very low temperature, was not competitive with closure of the biradical since acetophenone could only be detected in *c.* 2% yield. This contrasts with the photolysis of 1-phenylbutan-1-one[16] where fragmentation of the biradical intermediate is favoured (*c.* 9 : 1) to cyclization. The expected high energy of oxirene, a transitory product of the fragmentation reaction of epoxide (1a), probably accounts for the marked preference for cyclobutanol formation. Photolysis of *trans*-3,4-epoxy-1,4-diphenylbutan-1-one, where the phenyl substituent at C4 is capable of stabilizing an adjacent radical, gives a higher but still only modest yield[11] of products resulting from fragmentation.

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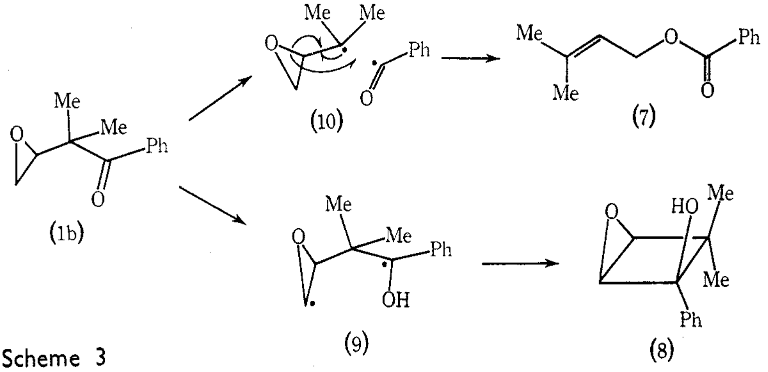
[15] Griffith, R. C., and Roberts, J. D., *Tetrahedron Lett.*, 1974, 3499.

[16] Lewis F. D., and Hilliard, T. A., *J. Am. Chem. Soc.*, 1970, **92**, 6672; 1972, **94**, 3852.

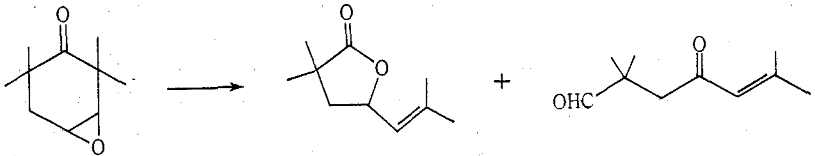
Photolysis of 3,4-epoxy-2,2-dimethyl-1-phenylbutan-1-one (1b) contrasts with that of the analogue (1a). Only two products and starting material were identified—a polar product was unstable and attempts to obtain a pure sample of this compound even at low temperatures were unsuccessful. The major product was isolated in only modest yield and identified as 3-methylbut-2-enyl benzoate (7) by comparison with an authentic sample. 2,3-Epoxy-4,4-dimethyl-1-phenylcyclobutan-1-ol (8) was formed in low yield (2%). The infrared spectrum showed the presence of the hydroxyl group and in the p.m.r. spectrum the methyls were present as singlets at δ 0·60 and 1·00, and the epoxide protons, centred at δ 4·17 and 3·57, were coupled to each other (*J* 2 Hz). The limited availability of this compound did not allow the relative stereochemistry at C 1 and C 2 to be unambiguously assigned. By analogy with the photolysis of epoxide (1a), the biradical intermediate (9) might be expected to undergo preferential rotation about the C 1–C 2 bond in a clockwise manner and result in the formation of the epoxycyclobutanol (8) with the oxygen substituents on the same face of the molecule (Scheme 3). The ester product, 3-methylbut-2-enyl benzoate (7), is envisaged to arise from α-cleavage (10) and such a process could be facilitated by the *gem*-dimethyl group. Bond formation between the radical fragments occurs between the oxygen of the oxyalkyl radical and the benzoyl radical.



Scheme 3

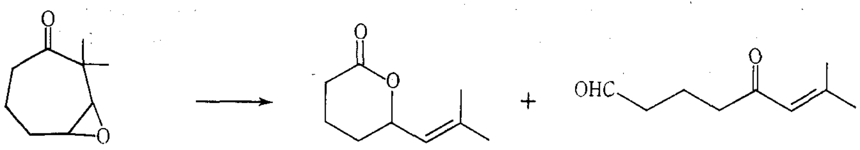
Lewis *et al.*[16] have observed a similar increase in the importance of α-cleavage with methyl substitution adjacent to the carbonyl for a series of substituted 1-phenylbutan-1-ones. In particular, for 2,2-dimethyl-1-phenylbutan-1-one the rate of α-cleavage is comparable with the rate of γ-hydrogen abstraction and this compares with 1-phenylbutan-1-one where α-cleavage is not competitive with γ-hydrogen transfer to the carbonyl. The increase in α-cleavage observed for epoxide (1b) compared with epoxide (1a) may result from either the increased stability of the epoxyalkyl radical fragment due to the presence of the methyl substituents, or from the greater steric strain between the C 1 and C 2 substituents in the starting epoxide. The formation of an ester product from photolysis of a β,γ-epoxy ketone is, however, not unprecedented;[9,10] 3,4-epoxy-2,2,6,6-tetramethylcyclohexanone (11)[10] (Scheme 4) on irradiation gives 3,3-dimethyl-5-(2-methylprop-1-enyl)-2,3,4,5-tetrahydrofuran-2-one (12) and the seven-membered ring analogue 3,4-epoxy-2,2-dimethylcycloheptanone (14) (Scheme 5) rearranges to 6-(2-methylprop-1-enyl)-1-oxacyclohexan-2-one (15). In both these reactions hydrogen abstraction by the acyl radical is competitive with lactone formation and 2,2,6-trimethyl-4-oxohept-5-enal (13) and

7-methyl-5-oxooct-6-enal (16) respectively are formed. The failure to detect benzaldehyde and or 3-methylbut-2-enal from photolysis of epoxide (1b) indicates that hydrogen abstraction by the benzoyl radical is not a competitive process. No products which would result from fragmentation of the 1,4-biradical could be detected and the isolation of only a trace of a cyclobutanol shows that α-cleavage is favoured over Norrish type II processes.



(11) (12) (13)

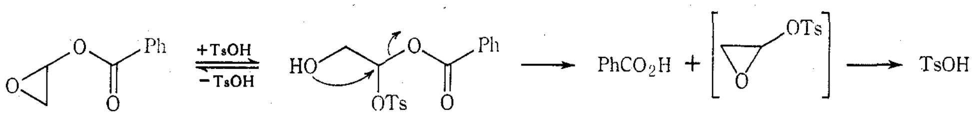
Scheme 4



(14) (15) (16)

Scheme 5

The C2-oxa analogue of epoxide (1a), namely oxiranyl benzoate (2), was unreactive to light (3000 and 2537 Å) in solution in benzene, pentane, acetonitrile and dichloromethane. When a solution of the epoxide (2) in dichloromethane was irradiated with 1849–2537 Å lamps, 1-chloro-2-hydroxyethyl benzoate was produced in high yield. The structure of the product was determined from the infrared spectrum, which showed hydroxyl and ester groups, and the p.m.r. spectrum. The C2 protons centred at δ 4·05 was coupled with C1–H centred at δ 6·72. Acetylation of the alcohol caused a downfield shift of $C2–H_2$ to δ 4·56. The C1–H is deshielded, but to a lesser extent, to δ 6·82. The greater shift of $C2–H_2$ on acetylation confirms that the chloride is at C1. In separate experiments it was shown that under the reaction conditions dichloromethane gives hydrogen chloride which adds to the epoxide in a ground state reaction. *p*-Toluenesulphonic acid also reacts with epoxide (2) to give an analogous product, 2-hydroxy-1-(*p*-toluenesulphonyl)ethyl benzoate (17). The orientation of the addition to the epoxide was confirmed by the effect on the chemical shift of C1–H and $C2–H_2$ on acetylation of the hydroxyl group. 2-Hydroxy-1-(*p*-toluenesulphonyl)ethyl benzoate (17) was unstable and decomposed (Scheme 6)



(2) (17)

Scheme 6

on standing to give a mixture from which benzoic acid and *p*-toluenesulphonic acid were isolated.

2,3-Epoxy-3-methylbutyl benzoate (3) was unreactive to light in solution with pentane or benzene. The unreactivity of both this ester and oxiranyl benzoate (2), on irradiation in inert solvents, is not surprising since it parallels observations made for photolysis of a series of alkyl esters.[17,18] The reason for their stability remains, however, a matter of debate.[19,20]

The photolysis of 1-phenylbutan-1-one and its alkyl derivatives give both Norrish type I and II photoproducts.[16] Fragmentation of the intermediate 1,4-biradicals in the type II process is often more than competitive with cyclobutanol formation. The high energy of oxirene, which would be a transitory product of fragmentation of the 1,4-biradicals formed from epoxide (1a) and (1b), is thought to account for the observed preference for cyclobutanol formation. The presence of a *gem*-dimethyl group adjacent to the carbonyl in compound (1b) increases the importance of Norrish type I reaction.

Experimental

Infrared spectra were recorded on a Shimadzu IR-27G spectrophotometer, ultraviolet spectra on a Shimadzu MPS-50L for ethanol solutions and p.m.r. spectra on a Varian A60 or T60 spectrometer for $CDCl_3$ solutions with $CHCl_3$ and Me_4Si as internal standards. Mass spectra were recorded on an A.E.I. MS902 spectrometer. Alumina used for chromatography was Spence grade H, deactivated by the addition of 5% v/v of 10% acetic acid. Silica gel was Sorbsil, B.S.C. grade. For dry column chromatography I.C.N. Pharmaceuticals silica gel Brockman activity III (30 mm) and neutral alumina activity III (20 mm) were used. Photolysis was carried out in a Rayonet photochemical reactor manufactured by the Southern New England Ultra Violet Company.

1-Phenylbut-3-en-1-ol

Freshly distilled 1-bromoprop-2-ene (48 g) in dry ether (60 ml) was slowly added to a vigorously, stirred mixture of magnesium turnings (10 g) and ether (225 ml) at −10° in a nitrogen atmosphere. After 2 h, a solution of benzaldehyde (40 g) in dry ether (60 ml) was added dropwise and the reaction mixture was kept at −10° for a further 2 h. A saturated solution of ammonium chloride was added and the product was extracted with ether, dried and after removal of solvent gave 1-phenylbut-3-en-1-ol, which was purified by vacuum distillation (70°, 75 mm) to yield 15 g of product. ν_{max} 3425, 1605 and 1592 cm^{-1}. λ_{max} (MeOH) 253·8 nm (ε 215), 256·7 (236) 263·5 (179). P.m.r. δ 7·32, s, C_6H_5; 6·18–4·85, C3–H and C4–H_2; 4·73, t, J 6·5 Hz, C1–H; 2·55, d of d, J 6·5 Hz, C2–H_2; 2·40, OH (Found: M^+, 148·0882. Calc. for $C_{10}H_{12}$: M^+, 148·0888).

3,4-Epoxy-1-phenylbutan-1-ol

To a solution of *m*-chloroperbenzoic acid (31·5 g) in anhydrous ether (1 l.) was added 1-phenylbut-3-en-1-ol (21 g) and the mixture was kept at room temperature for 2 weeks. Solid potassium carbonate was added and the mixture was filtered through alumina. After removal of solvent by distillation, the product was further purified by chromatography on deactivated alumina. Elution with light petroleum–ether (10 : 2) gave the *3,4-epoxy-1-phenylbutan-1-ols* (16 g). ν_{max} (film) 3460 cm^{-1}. λ_{max} (MeOH) 251 nm (ε 173), 257·5 (200), 263·7 (150). P.m.r. δ 7·28, s, C_6H_5; 4·80, $W_{h/2}$ 13 Hz; C1–H; 3·22, OH; 3·30–2·28, C3–H and C4–H_2; 1·88, $W_{h/2}$ 14 Hz, C2–H_2 (Found: M^+, 164·0833. $C_{10}H_{12}O_2$ requires M^+, 164·0837. Found: $M^+ - H_2O$, 146·0735. $C_{10}H_{10}O$ requires 146·0732). The sample decomposed when attempts were made to separate the isomers by preparative g.l.c.

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[17] Ausloos, P., *Can. J. Chem.*, 1958, **36**, 383.

[18] Barltrop, J. A., and Coyle, J. D., *J. Chem. Soc. B*, 1971, 251.

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[20] Coyle, J. D., and Kingston, D. H., *Tetrahedron Lett.*, 1975, 1021.

3,4-Epoxy-1-phenylbutan-1-one (1a)

A mixture of chromium trioxide (2 g) and anhydrous pyridine (3·16 g) was stirred for 20 min. A solution of 3,4-epoxy-1-phenylbutan-1-ols (0·54 g) in dichloromethane (1 ml) was added. A black tar formed, and the mixture was left for 30 min. The product was extracted by means of ether, washed with aqueous sodium bicarbonate and water, dried and after removal of solvent under reduced pressure at room temperature gave *3,4-epoxy-1-phenylbutan-1-one* (1a) (0·43 g). ν_{max} (film) 1686 cm^{-1}. λ_{max} (EtOH) 243 nm (ε 24400), 279 (10800), 328 (57). P.m.r. δ 7·90, $W_{h/2}$ 10 Hz and 7·50, $W_{h/2}$ 10 Hz, C_6H_5; 3·10–3·60, C3–H and C2–H_2; 2·87, $J_{4,4'}$ 5 Hz, $J_{4,3}$ 4 Hz, C4–H *cis* to C3–H; 2·55, $J_{4,4'}$ 5 Hz, $J_{4,3}$ 2·5 Hz, C4–H *trans* to C3–H. The sample decomposed in the inlet source of the mass spectrometer. On standing at 0° for 3–4 months 3,4-epoxy-1-phenylbutan-1-one rearranged to give a solid compound, which was recrystallized from methanol to give *4-hydroxy-1-phenylbut-2-en-1-one* (0·201 g), m.p. 69–71°. ν_{max} ($CHCl_3$) 3475, 1672 and 1623 cm^{-1}. λ_{max} (EtOH) 257·2 nm (ε 22000). P.m.r. δ 7·33–8·13, C_6H_5; 7·20, $W_{h/2}$ 2 Hz, C2–H and C3–H; 4·50, $J_{4,3}$ 2 Hz, C4–H_2, 2·08, $W_{h/2}$ 13 Hz, OH (Found: M$^+$, 162·0675. $C_{10}H_{10}O_2$ requires M$^+$, 162·0681). Treatment of 4-hydroxy-1-phenylbut-2-en-1-one with a trace of HCl (conc.) in methanol afforded 2-phenylfuran. P.m.r. δ 7·20–7·71, C_6H_5 and C5–H; 6·65, $J_{3,4}$ 2 Hz, C3–H; 6·45, J 4 Hz, J' 2 Hz, C4–H. [Lit.[21] p.m.r. δ 7·20–7·70, C_6H_5; 7·45, m, C5–H; 6·62, J 2 Hz, C3–H; 6·45, J 2 Hz, J' 4 Hz, C4–H.] Attempts to distil 3,4-epoxy-1-phenylbutan-1-one afforded 2-phenylfuran and therefore the photolysis studies were carried out on freshly prepared samples of the epoxide without further attempts to purify the substrate.

2,2-Dimethyl-1-phenylbut-3-en-1-ol

1-Bromo-3-methylbut-2-ene[21] (25 g) in anhydrous ether (50 ml) was added dropwise to a vigorously stirred mixture of magnesium turnings (8 g) in ether (100 ml) at 0° in a nitrogen atmosphere. After 3 h, the mixture was decanted and benzaldehyde (9 g) in ether was added to the solution. The resulting solution was stirred for 18 h at room temperature. A solution of saturated ammonium chloride was added and the product was extracted with ether, the solution was dried and the solvent was removed. The product was adsorbed onto deactivated alumina. Elution with light petroleum gave 2,2-dimethyl-1-phenylbut-3-en-1-one[22] (1·8 g). ν_{max} 1681, 1638 and 1603 cm^{-1}. λ_{max} (EtOH) 243·7 nm (ε 9200). P.m.r. δ 7·83 and 7·35, C_6H_5; 6·20, $J_{3,4cis}$ 10 Hz, $J_{3,4trans}$ 18 Hz, C3–H; 5·20, m, $W_{h/2}$ 20 Hz, C4–H_2; 1·40, 2CH_3 (Found: M$^+$, 174·1048. Calc. for $C_{12}H_{14}O$: M$^+$, 174·1045). Further elution with light petroleum–ether (5 : 1) gave 2,2-dimethyl-1-phenylbut-3-en-1-ol[14] (2·1 g). ν_{max} 3485 cm^{-1}. λ_{max} (EtOH) 247·2 nm (ε 344), 252 (358), 258 (309), 264·4 (211). P.m.r. δ 7·27, C_6H_5; 6·20–4·83, m, C3–H and C4–H_2; 4·37, $J_{H,OH}$ 3 Hz, C1–H; 2·13, $J_{OH,H}$ 3 Hz, OH; 1·00 and 0·95, 2CH_3 (Found: M$^+$, 176·1202. Calc. for $C_{12}H_{16}O$: M$^+$, 176·1201). Elution with light petroleum–ether (5 : 2) gave benzyl alcohol (1·5 g). ν_{max} (film) 3355 cm^{-1}. P.m.r. δ 7·30 (C_6H_5); 4·55, $W_{h/2}$ 6 Hz, CH_2OH; 2·87, OH.

3,4-Epoxy-2,2-dimethyl-1-phenylbutan-1-ols

To 2,2-dimethyl-1-phenylbut-3-en-1-ol (0·52 g) in ether (50 ml) was added *m*-chloroperbenzoic acid (1·10 g) and the resulting solution was kept at room temperature for 1 week. The product was isolated in the usual manner and adsorbed onto deactivated alumina. Elution with light petroleum–ether (10 : 2) gave a mixture of the isomeric *3,4-epoxy-2,2-dimethyl-1-phenylbutan-1-ols* (0·40 g). ν_{max} (film) 3455 cm^{-1}. λ_{max} (EtOH) 247·3 nm (ε 169), 252·1 (199), 258·1 (212), 264·2 (52). P.m.r. δ 7·30, $W_{h/2}$ 3 Hz, C_6H_5; 4·55, J 2 Hz, C1–H of one isomer; 4·48, J 2 Hz, C1–H of the other isomer; 2·88, $W_{h/2}$ 14 Hz, C3–H and OH; 2·57, $W_{h/2}$ 12 Hz, C4–H_2; 0·80 (2CH_3 of one isomer), 0·83 and 0·75 (2CH_3 of other isomer) (Found: C, 75·2; H, 8·5; M$^+$, 192·1142. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%; M$^+$, 192·1150).

3,4-Epoxy-2,2-dimethyl-1-phenylbutan-1-one (1b)

A mixture of chromium trioxide (1·5 g), anhydrous pyridine (2·38 g) and dichloromethane (40 ml) was stirred for 20 min. A solution of 3,4-epoxy-2,2-dimethyl-1-phenylbutan-1-ols (500 mg) in

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[21] Ayres, D. C., and Smith, J. R., *J. Chem. Soc. C*, 1968, 2737.

[22] Birch, A. J., Corrie, J. E. T., and Subba Rao, G. S. R., *Aust. J. Chem.*, 1970, **23**, 1811.

dichloromethane (0·5 ml) was added and the mixture was kept for 30 min. Isolation of the product in the usual manner afforded *3,4-epoxy-2,2-dimethyl-1-phenylbutan-1-one* (1b) (440 mg). ν_{max} 1681, 1606 and 1584 cm^{-1}. λ_{max} (EtOH) 244·2 nm (ε 8000), 278·5 (760), 323 (138). P.m.r. δ 7·87 and 7·43, C_6H_5; 3·20, J 3 Hz, J' 4·5 Hz, C3–H; 2·80, $W_{h/2}$ 7 Hz, C4–H_2; 1·28, $2CH_3$ (Found: M$^+$, 190·0993. $C_{12}H_{14}O_2$ requires M$^+$, 190·0994) (Found: C, 75·4; H, 7·3. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

Oxiranyl Benzoate (*2*)

Ethenyl acetate (34·5 g), benzoic acid (18·5 g), mercuric acetate (0·5 g) and sulphuric acid (conc. 0·5 ml) were heated until the temperature reached 140°. Fractional distillation afforded ethenyl benzoate. ν_{max} 1737 and 1647 cm^{-1}. P.m.r. δ 8·20–7·33, C_6H_5; 5·03, J 14·0 Hz, J' 1·5 Hz, C2–H *cis* to benzoate; 4·65, J 7 Hz, J' 1·5 Hz, C2–H *trans* to benzoate (Found: M$^+$, 148·0522. Calc. for $C_9H_8O_2$: M$^+$, 148·0524). Ethenyl benzoate (1·0 g) was dissolved in dry dichloromethane (60 ml) and *m*-chloroperbenzoic acid (2·6 g) added. The reaction mixture was kept at room temperature for 7 days. Potassium carbonate crystals were added and the mixture was stirred for 10 min. The mixture was rapidly filtered through a column containing alumina (50 g) assisted by suction. The column was washed with ether, and the combined extracts were distilled under reduced pressure to give benzoate (2) (700 mg). ν_{max} 1735 cm^{-1}. P.m.r. δ 8·01–7·40, C_6H_5; 5·80, J 2·5 Hz, J' 1·0 Hz, C1–H; 2·97, $W_{h/2}$ 9 Hz, C2–H_2 (Found: M$^+$, 164·0470. Calc. for $C_9H_8O_3$: M$^+$, 164·0473).

2,3-Epoxy-3-methylbutyl Benzoate (*3*)

1-Bromo-3-methylbut-2-ene[23] (12 g) and sodium benzoate (9·6 g) in benzene (60 ml) were heated under reflux for 12 h. The mixture was filtered and after removal of the solvent by distillation the residue was adsorbed onto deactivated alumina (200 g). Elution with light petroleum gave 3-methylbut-2-enyl benzoate[24] (2·6 g). ν_{max} 1723 cm^{-1}. λ_{max} (EtOH) 229·2 nm (ε 13000). P.m.r. δ 7·97 and 7·50, C_6H_5; 5·47, complex t, J 7 Hz, $J_{H,Me}$ values small, C2–H; 4·80, J 7 Hz, C1–H_2; 1·78, C4–H_3 and C3–CH_3. A solution of 3-methylbut-2-enyl benzoate (0·5 g) in ether (50 ml) was added to a solution of *m*-chloroperbenzoic acid (1·0 g) in ether (50 ml) and the resulting mixture was heated under reflux for 2½ h. The reaction was quenched by the addition of excess of anhydrous potassium carbonate. The solid was removed by filtration and the solvent was removed under vacuum. The crude product was adsorbed into deactivated alumina (20 g). Elution with light petroleum–ether (5 : 1) gave 2,3-epoxy-3-methylbutyl benzoate (3) (1·3 g). ν_{max} 1723 cm^{-1}. P.m.r. 8·23–7·4, C_6H_5; 4·60, J 12·5 Hz, J' 4·5 Hz, C1–H; 4·34, J 12·5 Hz, J' 6·5 Hz, C1–H; 3·13, J 4·5 Hz, J' 6·5 Hz, C2–H; 1·38, C4–H_3 and C3–CH_3.

Photolysis

(i) (*3*RS)-*3,4-Epoxy-1-phenylbutan-1-one* (*1a*).—A solution of (3*RS*)-3,4-epoxy-1-phenylbutan-1-one (125 mg) in anhydrous degassed benzene (125 ml) in a Pyrex vessel under a nitrogen atmosphere was irradiated (3000 Å) and the reaction was monitored by t.l.c. After 19 h, the solvent was removed and the residue was adsorbed onto deactivated alumina. Elution with light petroleum–ether (10 : 1) gave (*1*RS,*2*RS,*3*RS)-*2,3-epoxy-1-phenylcyclobutan-1-ol* (4) (59 mg). ν_{max} (CCl_4) 3600 and 3530 cm^{-1}. λ_{max} (EtOH) 252·2 nm (ε 235), 258·5 (238), 265 (172). P.m.r. δ 7·33, $W_{h/2}$ 22 Hz, C_6H_5; 3·99, $J_{2,3}$ 2 Hz, $J_{2,4c}$* 2 Hz, C2–H; 3·95, $J_{3,2}$ 2 Hz, C3–H; 2·92 $W_{h/2}$ 2 Hz, OH; 2·50, $J_{4c,4t}$ 12·5 Hz, C4*t*–H; 2·02, $J_{4c,4t}$ 12·5 Hz, $J_{4,2}$ 2 Hz, C4*c*–H. After addition of Eu(fod)$_3$: δ 8·4, $W_{h/2}$ 12 Hz and 7·55, $W_{h/2}$ 14 Hz, C_6H_5; 6·12, $J_{2,3}$ 1 Hz, $J_{2,4c}$ 2 Hz, C2–H; 5·72, $J_{3,2}$ 2 Hz, C3–H; 4·27, $J_{4c,4t}$ 12·75 Hz, $J_{4,2}$ 2 Hz, C4*c*–H; 3·96, $J_{4c,4t}$ 12·75 Hz, C4*t*–H (Found: M$^+$, 162·0674. $C_{10}H_{10}O_2$ requires M$^+$, 162·0681). Further elution with light petroleum–ether 10 : 1 gave (*1*RS,*2*SR,*3*SR)-*2,3-epoxy-1-phenylcyclobutan-1-ol* (5) (35 mg) recrystallized from methanol as needles, m.p. 54–55°. ν_{max} (CCl_4) 3620 and 3475 cm^{-1}. λ_{max} (EtOH) 252 nm (ε 185), 258 (205), 264·4 (151). P.m.r. δ 7·30, $W_{h/2}$ 5 Hz, C_6H_5; 3·90, $W_{h/2}$ 3 Hz, C2–H and C3–H; 2·27, $W_{h/2}$

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* In the description of the n.m.r. spectra 4*c* refers to the C4–H *cis* to the hydroxyl, and 4*t* to the other.

[23] Staudinger, H., Kreis, W., and Schilt, W., *Helv. Chim. Acta*, 1922, **5**, 743.

[24] Maguet, L., and Lerer, M., *Bull. Soc. Chim. Fr.*, 1965, 3262.

3 Hz, C4–H_2; 2·02, $W_{h/2}$ 12 Hz, OH. After addition of Eu(fod)$_3$: δ 9·0, $W_{h/2}$ 10 Hz and 7·52, $W_{h/2}$ 9 Hz, C_6H_5; 6·03, $J_{2,3}$ 2 Hz, $J_{2,4c}$ 2 Hz, C2–H; 5·55, $J_{3,2}$ 2 Hz, C3–H; 3·78, $J_{4c,4t}$ 12 Hz, $J_{4,2}$ 2 Hz, C4*c*–H; 3·43, $J_{4c,4t}$ 12 Hz, C4*t*–H (Found: M^+, 162·0679. $C_{10}H_{10}O_2$ requires M^+, 162·0681). The crude reaction product was examined by g.l.c. (Carbowax 20 M and SE 30) and a trace compound (*c.* 2%) having the same retention as acetophenone was detected.

(ii) *3,4-Epoxy-2,2-dimethyl-1-phenylbutan-1-one* (*1b*).—3,4-Epoxy-2,2-dimethyl-1-phenylbutan-1-one (550 mg), dissolved in anhydrous degassed benzene (300 ml) in a Pyrex vessel under a nitrogen atmosphere, was photolysed (3000 Å) and the reaction progress was monitored by t.l.c. After 4½ h, three spots could be detected by t.l.c. on alumina. Chromatography on deactivated alumina gave on elution with light petroleum 3-methylbut-1-enyl benzoate (7) (56 mg). ν_{max} 1723 cm^{-1}. λ_{max} (EtOH) 229·2 nm (ε 13000). P.m.r. δ 7·97 and 7·50, C_6H_5; 5·47, t, J 7 Hz, C2–H; 4·80, J 7 Hz, C1–H_2; 1·78, C4–H_3 and C3–CH_3 (Found: M^+ 190·0996. Calc. for $C_{12}H_{14}O_2$: M^+, 190·0994). Further elution with light petroleum gave mixed fractions of 3-methylbut-2-enyl benzoate (7) and 3,4-epoxy-2,2-dimethyl-1-phenylbutan-1-one (30 mg) which were not separable by t.l.c. on alumina and constitute the components of the least polar spot of the reaction mixture. Elution with light petroleum–ether (20 : 1) gave *2,3-epoxy-4,4-dimethyl-1-phenylcyclobutan-1-ol* (8) (11 mg) which crystallized as needles from methanol, m.p. 98–100°. ν_{max} ($CHCl_3$) 3575 cm^{-1}. P.m.r. δ 7·27, $W_{h/2}$ 3 Hz, C_6H_5; 4·17 and 3·57, $J_{2,3}$ 2 Hz, C2–H and C3–H; 2·68, $W_{h/2}$ 6 Hz, OH; 1·00 and 0·60 (2CH_3). Repeated attempts to isolate the more polar reaction product failed. The compound rapidly decomposed on alumina even at 0°.

(iii) *Oxiranyl benzoate* (*2*).—Oxiranyl benzoate (0·2% w/v) dissolved in anhydrous benzene was irradiated (3000 Å) in a Pyrex vessel under a nitrogen atmosphere for 22 h and the progress of the reaction was monitored by p.m.r. No reaction could be detected. Solutions of oxiranyl benzoate in pentane, acetonitrile and dichloromethane were irradiated (2537 Å) in quartz vessels for 22 h but no reaction could be detected by p.m.r. Photolysis of oxiranyl benzoate (120 mg) in dichloromethane (100 ml) in a quartz vessel by means of 1849–2537 Å lamps for 8 h gave *1-chloro-2-hydroxymethyl benzoate* (130 mg). ν_{max} 3450, 1742 and 1250 cm^{-1}. P.m.r. δ 8·20–7·34, C_6H_5; 6·72, t, J 5·5 Hz, C1–H; 4·87, $W_{h/2}$ 15 Hz, OH; 4·05, d, J 5·5 Hz, C2–H_2. To a solution of 1-chloro-2-hydroxyethyl benzoate (100 mg) in chloroform (5 ml) was added *N,N*-dimethylaniline (200 mg) and acetyl chloride (140 mg) and the mixture stirred at room temperature for 5½ h.[25] The mixture was diluted by the addition of dichloromethane and washed successively with dilute aqueous sulphuric acid, saturated sodium bicarbonate and water. The organic phase was dried with anhydrous magnesium sulphate and the solvent was removed to give *2-acetoxy-1-chloroethyl benzoate* (98 mg). ν_{max} (film) 1750 and 1230 cm^{-1}. P.m.r. δ 7·43–8·22, C_6H_5; 6·82, t, J 6 Hz, C1–H; 4·56, J 6 Hz, C2–H_2; 2·08, OAc (Found: M^+, 242·0337. $C_{11}H_{11}{}^{35}ClO_4$ requires M^+, 242·0346).

(iv) *2,3-Epoxy-3-methylbutyl benzoate* (*3*).—Solutions of 2,3-epoxy-3-methylbutyl benzoate (0·1% w/v) in benzene and in pentane (3000 and 2537 Å) were irradiated for up to 2 days after which time no reaction could be detected.

Reaction of Oxiranyl Benzoate with p-*Toluenesulphonic Acid*

A solution of oxiranyl benzoate (100 mg) and *p*-toluenesulphonic acid (120 mg) in ether was kept at room temperature for 3½h. An aqueous solution of potassium carbonate was added and after the mixture had been stirred for 15 min, anhydrous potassium carbonate and magnesium sulphate were added. After filtration and removal of the solvent, the residue was identified as *2-hydroxy-1-*(p-*toluenesulphonyl*)*ethyl benzoate* (17) (120 mg). ν_{max} (film) 3520, 1735, 1355 and 1235 cm^{-1}. P.m.r. δ 8·23–7·10, C_6H_5 and C_6H_4; 6·88, t, J 4·5 Hz, C1–H; 3·90, d, J 4·5 Hz, C2–H_2; 3·28, $W_{h/2}$ 12 Hz, OH; 2·20, $C_6H_4CH_3$. The compound decomposed both in the inlet of the mass spectrometer and on standing overnight. Benzoic acid was isolated by extraction with $CHCl_3$. The residue was identified as *p*-toluenesulphonic acid. Reaction of oxiranyl benzoate with catalytic quantities of *p*-toluenesulphonic acid for 3½ h gave a mixture from which starting oxiran and 2-hydroxy-1-(*p*-toluenesulphonyl)ethyl benzoate were isolated but after 12 h no starting material could be detected and benzoic acid was isolated.

To a solution of freshly prepared 2-hydroxy-1-(*p*-toluenesulphonyl)ethyl benzoate in chloroform (5 ml) was added *N,N*-dimethylaniline (200 ml) and acetyl chloride (140 mg) and the solution was

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[25] Plattner, P. A. von, Petrzilka, T., and Lang, W., *Helv. Chim. Acta*, 1944, **27**, 513.

stirred at room temperature for 5½ h.[25] The product was isolated in the usual manner to give *2-acetoxy-1-*(p-*toluenesulphonyl*)*ethyl benzoate*. P.m.r. δ 8·40–7·07, C_6H_5 and C_6H_4; 6·85, t, J 5 Hz, C1–H; 4·58, d, J 5 Hz, C2–H_2; 3·28, $C_6H_4CH_3$; 2·08 (OAc) (the compound decomposed in the inlet of mass spectrometer).

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