Photochemistry of 2,3-Epoxy-3-phenylpropiophenones

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Irradiation of 2,3-epoxy-3-phenylpropiophenones causes rearrangement to dibenzoylmethanes, *trans* ⟶ *cis*-isomerisation, and photofragmentation *via* acylcarbene intermediates. Photophysical studies show that the lowest excited state is a (π^*,n) state.

In an early photochemical investigation, Bodforss[1] showed that 2,3-epoxy-3-phenylpropiophenones (chalcone oxides) gave low yields of the corresponding 1,3-diphenylpropane-1,3-diones (dibenzoylmethanes). This apparent 1,2-shift has been observed by other workers[2-4] with related epoxy-ketones, and more recently by Kagan[5] with the elusive 2′-hydroxychalcone. These studies have been briefly reviewed along with the more extensive photochemistry of the simple oxiran system.[6-8] The role of chalcone oxides or a closely related ' oxidized chalcone ' is a major problem in flavonoid biosynthesis,[9,10] as is the fact that anthocyanins are formed in many plants only in the presence of light whereas the closely related flavanols can be synthesized in the dark.[11] Hence a more detailed photochemical investigation of chalcone oxides was undertaken with regard to the possibility of non-enzymic conversion of these epoxides into natural products.

EXPERIMENTAL

I.r. spectra were measured with a Beckman IR8 instrument, u.v. spectra with a Cary 14 or a Beckman DB-9 spectrophotometer, and ^1H n.m.r. spectra with a Varian T60 or HA 100 spectrometer. Fluorescence and phosphorescence analysis were carried out with an Aminco–Bowman spectrophotofluorometer with phosphoroscope attachement. Mass spectra were measured with an A.E.I. MS 12 instrument. All photoreactions were carried out with a Rayonet Photochemical Chamber reactor, using 253.7 nm low-pressure mercury lamps.

(a) *Epoxidation of Chalcones.*—*trans*-Chalcone oxide (1) and *trans*-2-methoxychalcone oxide (2) were prepared by the method of Black and Lutz[12] in 80 and 65% yield, respectively. All attempts at epoxidizing 2-hydroxychalcone were unsuccessful.

(b) 1,3-*Diphenylpropane*-1,2-*dione* (3).—This was pre-

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[1] S. Bodforss, *Ber.*, 1918, **51**, 214.

[2] C. S. Markos and J. Reusch, *J. Amer. Chem. Soc.*, 1967, **89**, 3363.

[3] H. E. Zimmerman, B. R. Cowley, C. Y. Tseng, and J. W. Wilson, *J. Amer. Chem. Soc.*, 1964, **86**, 947.

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[5] V. T. Ramakrishnan and J. Kagan, *J. Org. Chem.*, 1970, **35**, 2898.

[6] A. Padwa in ' Organic Photochemistry,' vol. 1, Dekker, New York, 1967, p. 97; *Accounts Chem. Res.*, 1971, **4**, 48.

[7] A. P. Meleshevich, *Russ. Chem. Rev.*, 1970, **39**, 213.

[8] N. R. Bertoniere and G. W. Griffin in ' Organic Photochemistry,' vol. 3, Dekker, New York, 1973, p. 116.

[9] T. A. Geissman, and D. Fukushima, *J. Amer. Chem. Soc.*, 1948, **70**, 1686.

[10] F. M. Dean and V. Podimuang, *J. Chem. Soc.*, 1965, 3978.

[11] H. Grisebach in ' Chemistry and Biochemistry of Plant Pigments,' Academic Press, New York, 1965.

[12] W. B. Black and R. E. Lutz, *J. Amer. Chem. Soc.*, 1953, **75**, 5990

pared from chalcone oxide as described by Barnes and Chigbo;[13] 3-(2-methoxyphenyl)-1-phenylpropane-1,2-dione (4) was prepared similarly.

(c) 1-(2-*Methoxyphenyl*)-3-*phenylpropane*-1,3-*dione* (6).—1-(2-Hydroxyphenyl)-3-phenylpropane-1,3-dione (0.1 g) was dissolved in ether, and cold ethereal diazomethane (10 cm^3 containing *ca.* 18 mg cm^{-3}) was added at 0 °C. After 1 h, nitrogen was bubbled through and the solvent removed before chromatography of the yellow oil through a 750 × 20 mm column of polyamide [light petroleum–butanone–methanol (90 : 5 : 5) as eluant]. Two components were eluted, the first being tentatively identified as (6); the second was starting material.

(d) *Photolysis of* trans-*Chalcone Oxide*.—The epoxide (0.224 g) was dissolved in ethanol, methanol, or benzene (10 cm^3) in a 20 mm quartz tube, and the solution flushed with nitrogen and then irradiated for 2.5 h. The solution temperature was maintained at 15—16 °C by use of a ' cold finger '. Solvent was then removed below 35 °C. Blank runs in the dark showed no decomposition at 30 °C over 3 h.

(e) *Product Analysis*.—(i) For g.l.c., an Aerograph 202 thermal conductivity instrument was used with the following columns: 3 ft × $\frac{1}{4}$ in 10% SE30, 3 ft × $\frac{1}{4}$ in 10% polyamide 103, and 8 ft × $\frac{1}{4}$ in 10% SE30, all on DMCS-AW Chromosorb W. Low molecular weight fragments were analysed on 8 ft columns with column temperature 140—160 °C, injector temperature, 175 °C, and flow rate 80 ml min^{-1}; no fragmentation of the starting materials occurred under these conditions. Higher temperatures and a flow rate of 100—200 ml min^{-1} were required with the polyamide column. The epoxide was eluted at 200 °C and a flow rate of 80 ml min^{-1}, but thermal breakdown was marked at this temperature.

(ii) T.l.c. was carried out on the photolysates; both silica gel and polyamide adsorbents were utilised. Benzene–acetone (9 : 1) was the most common developing solvent used with silica gel; light petroleum–benzene–butanone–methanol (60 : 30 : 5 : 5) was used on polyamide plates, which generally gave better separations.

(iii) Column chromatography was usually performed on silica gel, and the fractions were analysed by g.l.c., t.l.c., and n.m.r., u.v., and mass spectrometry. The crude photolysates were also monitored by n.m.r. to ensure that no major decomposition occurred during chromatography.

(f) *Product Identification*.—The products from *trans*-chalcone oxide (Table 1) were identified by ^{1}H n.m.r., mass, and u.v. spectral data. Where possible the data were compared with those obtained from authentic samples. The n.m.r. spectrum of *cis*-chalcone oxide showed the characteristic AB doublet for the oxiran ring protons [δ 3.88 and 4.36 (J 1.2 Hz); *cf.* 4.05 and 5.25 (J 2 Hz) for the *trans*-isomer]. 3-Hydroxy-1,3-diphenylpropan-1-one was identified on the basis of its mass spectrum, which showed a parent ion *m/e* 226 with other major peaks at $M - 2$, $M - 105$ (PhCO), $M - 121$ (PhCHOHCH$_2$), and *m/e* 77, with a small $M - 18$ (H$_2$O) peak.

TABLE 1

Products from irradiation of *trans*-chalcone oxide

Compound	Yield (%) in methanol	Yield (%) in benzene
trans-Chalcone oxide	35	20
cis-Chalcone oxide		20
1,3-Diphenylpropane-1,3-dione	18	20
Benzaldehyde Benzoic acid	20	25
3-Hydroxy-1,3-diphenylpropan-1-one	<1	
2-Phenylacetaldehyde	Trace	

(g) *Photoreactions of* 1,3-*Diphenylpropane*-1,3-*dione* (5) *and* 1,3-*Diphenylpropane*-1,2-*dione* (3) *at* 253.7 *nm*.—These compounds were irradiated as in section (d) to determine whether any of the products arose by secondary photoreactions of these materials, but none of the photofragmentation products were obtained.

(h) *Photoreaction of* 2-*Methoxychalcone Oxide* (2).—The epoxide (0.1 g) was irradiated in methanol or benzene (10 cm^3) at 253.7 nm as described for chalcone oxide except that the reaction time was 0.75 h. The photoreactions in methanol were carried out at 15 °C, room temperature, and 40 °C, but the increase in temperature had no effect on products or yields. Acetophenone, 2-methoxybenzaldehyde, and methyl 2-methoxybenzoate were identified by comparison with authentic samples. Compound (7) had *m/e* 286, which indicates the addition of CH$_3$OH to the epoxide, and the proposed structure is consistent with C$_\alpha$–O cleavage of the oxiran ring. At the temperatures necessary to elute 3-(2-methoxyphenyl)-1-phenylpropane-1,2-dione and 1-(2-methoxyphenyl)-3-phenylpropane-1,3-dione, the oxiran is cleaved to a diketone which has the same retention time as the compound formulated as 1-(2-methoxyphenyl)-3-phenylpropane-1,3-dione. The unknown (A), which is yellow, decomposes on isolation to give benzaldehyde, then benzoic acid. No molecular weight was obtained for this product.

TABLE 2

Products from the photoreactions of 2-methoxychalcone oxide

Compound	Yield (%) in methanol	Yield (%) in benzene
Unknown (A) (+ acetophenone)	5 (4) [5]	9
2-Methoxybenzaldehyde	4 (13) [6]	24
Methyl 2-methoxybenzoate	5 (3) [3]	
3-(2-Methoxyphenyl)-1-phenylpropane-1,2-dione + 1-(2-methoxyphenyl)-3-phenylpropane-1,3-dione	25 [17) [31]	38
Hydroxy-ketone (7)	24 (24)	
2-Methoxychalcone oxide	32 (39) [55]	24
Unknown (B)	5 (0)	5

* Yields in parentheses obtained at 350 nm; yields in square brackets obtained with added dimethyl but-2-ynedioate.

(i) *Photoreaction in the Presence of Dimethyl But*-2-*ynedioate in Methanol*.—Dimethyl but-2-ynedioate was added in the hope that it would either act as an ene component in a photochemical Diels–Alder reaction or trap 1,3-dipolar imtermediates.[14] Its primary effect was to inhibit the formation of the hydroxy-ketone (7) and the unknown (B). Fragmentation product yields were essentially unchanged. However the major products resulted from the addition of methanol to the acetylene to give *cis*- and *trans*-dimethyl 2-methoxybut-2-enedioate, *m/e* 174, in high yield. Irradiation of the acetylene alone in methanol gave only traces of these compounds. The photochemical addition of methanol to diphenylacetylene has been reported to give a 20% yield of the *trans*-adduct after 10 h.[15]

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[13] R. P. Barnes and F. E. Chigbo, *J. Org. Chem.*, 1963, **28**, 1644.

[14] R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565.

[15] T. D. Roberts, H. Schechter, and L. Ardemagni, *J. Amer. Chem. Soc.*, 1969, **91**, 6185.

(j) *Photoreactions of the Diones* (4) *and* (6) *at* 253.7 *nm.*—No low molecular weight products were obtained from the photoreactions of either dione.

(k) *U.v. Absorption Studies.*—The effects of solvent on the positions of absorption maxima are recorded in Table 3.

TABLE 3

Compound	Solvent	λ/nm (ε/l mol^{-1} cm^{-1})
Chalcone oxide	Ethanol	317.5 (280), 250 (16 600)
	1,4-Dioxan	323.5, 250
	Cyclohexane	353 (110), 337.5 (160), 326.5infl (160), 285sh (1 200), 246.5 (17 200)
2-Methoxychalcone oxide	Ethanol	335infl (680), 284 (5 700), 250 (14 600), 224infl (11 400)
	1,4-Dioxan	335, 284, 250
	Cyclohexane	333.5 (500), 282 (5 800), 245 (15 300)

(l) *Fluorescence and Phosphorescence Studies.*—No fluorescence was observed for either epoxide. The data obtained from phosphorescence spectra are included in Table 4.

TABLE 4

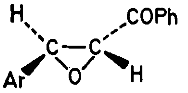
Phosphorescence spectra

Compound	Nature of spectrum	$\lambda_{max.}$/nm	Energy (kcal mol^{-1})
Chalcone oxide (1)	Emission	431	66
		460—465infl	62
	Excitation	255sh	112
		305sh	94
		358	80
2-Methoxychalcone oxide (2)	Emission	436	66
	Excitation	255	112
		320	90
		360sh	80

Coloured species resulted from irradiation of the epoxides at 77 K (purple-mauve for chalcone oxide and deep navy blue for the 2-methoxy-derivative). Irradiation at any excitation wavelength gave this result, the colour being more intense at longer wavelengths and disappearing on warming; it could be brought back by cooling and re-irradiating.

DISCUSSION

Photoreactions of chalcone oxide and its 2-methoxy-derivative at 253.7 nm involve initial excitation to a $^1(\pi^*, \pi)$ state, which undergoes internal conversion to a lower energy $^1(\pi^*, \pi)$ state. Two major processes could then occur: intersystem crossing to a $^3(\pi^*, \pi)$ triplet, or internal conversion to a lower energy $^1(\pi^*, n)$ state, the former process predominating. The absence of fluorescence from the $^1(\pi^*, n)$ state means either that there is very fast intersystem crossing or that quenching processes to the ground state are very fast. The presence of phosphorescence spectra proves that intersystem crossing does occur and that the triplet state can revert to the ground state or undergo photoreaction.



(1) Ar = Ph

(2) Ar = 2-MeO·C_6H_4

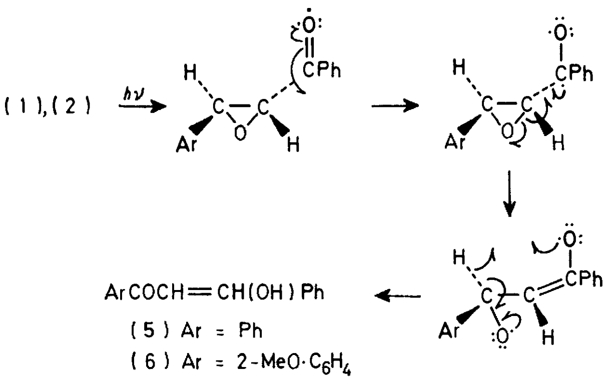
ArCH=C(OH)·COPh

(3) Ar = Ph

(4) Ar = 2-MeO·C_6H_4

The energy level of the lower $^1(\pi^*, n)$ state 0–0 band of the epoxide (1) is *ca.* 80—90 kcal mol^{-1}; the triplet energy is in the range 66—76 kcal mol^{-1}; these ranges do not permit distinguishing the configuration of the triplet state, but the difference between the singlet and triplet levels is similar to that found for unsaturated carbonyl compounds [16] with $^3(\pi^*, n)$ lowest states, and the triplet energies observed are in the same range as those which have lowest $^3(\pi^*, n)$ states.[17] The spectra of 2-methoxychalcone epoxide is similar but its second $^1(\pi^*, \pi)$ band is red shifted and appears as a distinct absorption. 0–0 Band energies are in the range 73—85 kcal mol^{-1} for the $^1(\pi^*, n)$ state and 65—77 kcal mol^{-1} for the triplet, and it appears that both the lowest singlet and triplet excited states in methanol have a $^1(\pi^*, n)$ configuration; the absence of *cis–trans*-isomerisation is another indication of a lowest $^3(\pi^*, n)$ state.

The photochemical processes observed in this study were rearrangement to dibenzoylmethanes, *trans* ⟶ *cis* isomerisation, and photofragmentation. The first process has been known since 1918, when Bodforss observed the formation of dibenzoylmethane from chalcone oxide in low yield. In this work and that of Kagan [5] it is a major product. The formation of β-diketones has been described as resulting from a C_α–O bond fission followed by a C_β-substituent 1,2-shift. However these β-diketones exist *ca.* 90% in the enolic form,[18] and so a mechanism similar to that suggested by Zimmerman for the formation of the hydroxy-ketone (9) from *trans* dypnone oxide (8) seems more likely (Scheme 1), *i.e.* the hydrogen shifts to oxygen not carbon as a result of (π^*, n) excitation. If C_α–O bond fission were the key step then some *cis*-chalcone oxide should have resulted, owing to rotation around the C_α–C_β bond. That the *cis*-epoxide was not found here, although it was isolated in other experiments, is good evidence for a hydrogen-transfer mechanism. It is not clear whether a singlet or



SCHEME 1

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[16] (*a*) S. P. McGlyn, I. Azumi, and M. Kinoshita, 'Molecular Spectroscopy of the Triplet State,' Prentice-Hall, New Jersey, 1969; (*b*) N. J. Turro, 'Molecular Photochemistry,' Benjamin, New York, 1967

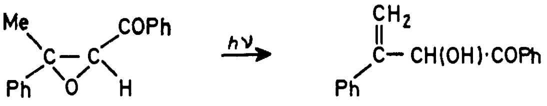
[17] J. S. Swenton, *J. Chem. Educ.*, 1969, **46**, 217.

[18] E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, Rinehart, and Winston, New York, 1959.

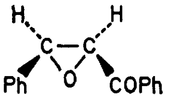
a triplet (π^*, n) state is responsible for dibenzoylmethane formation; Markos and Reusch's study[2] on aliphatic epoxy-ketones showed that the singlet state was involved in 1,3-diketone formation, whereas our emission spectra suggest a triplet state.

ArCH(OH)·CH(OMe)·COPh

(7) Ar = 2-MeO·C_6H_4



(8) (9)



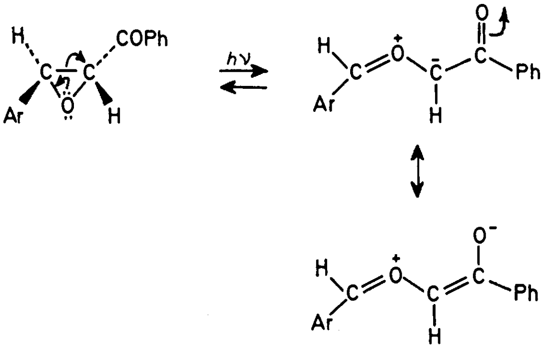
(10)

PhCH(OH)·CH_2·COPh

(11)

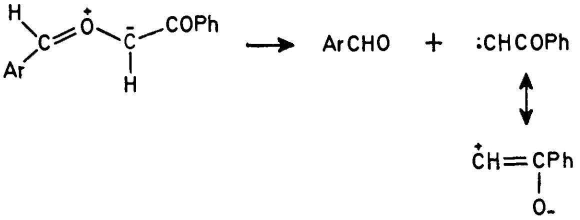
In benzene some *cis*-epoxide (10) was formed from *trans*-chalcone oxide; this reaction almost certainly involves the $^3(\pi^*, \pi)$ state. Another indication that a different pathway is implicated is that the *cis*-epoxide is formed in a substantial yield without any decrease in dibenzoylmethane formation. It is possible that in benzene the energy level of the $^3(\pi^*, \pi)$ state has been lowered sufficiently for it to compete with the $^3(\pi^*, \pi)$ state.

Photofragmentation has not been reported previously in this series. Benzoic acid can be considered to arise from the first-formed aldehyde by aerial oxidation. The formation of aldehydes is analogous to the breakdown of oxirans observed by Griffin,[19] and the similarity is reinforced by the observation of coloured intermediates like those reported to be formed upon irradiation of phenyloxiran in rigid glasses at 77 K.[20] A similar intermediate could be formed from the chalcone oxides, and this can be further stabilized by resonance interactions with the benzoyl function (Scheme 2). Cleavage of this intermediate would lead to benzaldehyde and 2-methoxybenzaldehyde, and an acylcarbene which would form complex products if it reacted in the dipolar form (Scheme 3). The fact that 2-methoxychalcone oxide gives 2-methoxybenzaldehyde is further evidence that the C_α–O bond is opened in the reaction; indeed, there is a strong resemblance between the reactions of chalcone oxides and those of methyl 2,3-diphenyloxiran-2-carboxylate, which gives benzaldehyde and methoxycarbonyl(phenyl)carbene.[21]

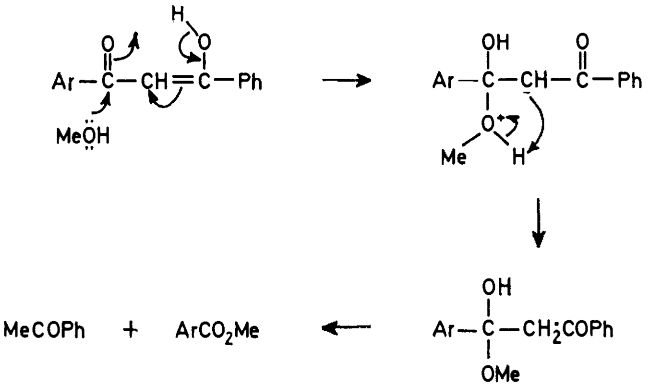


SCHEME 2

The formation of acetophenone and methyl 2-methoxybenzoate can be best rationalized in terms of fragmentation of the product of addition of methanol to (6) (Scheme 4). Likewise the hydroxy-ketone (7) arises from the addition of methanol to (2) after C_α–O cleavage, and the formation of these compounds must be responsible in part for the decreased yields of (6) in methanol. 3-Hydroxy-1,3-diphenylpropan-1-one (11) must result from abstraction of hydrogen from the solvent, and its presence is further evidence for a (π^*, n) state.



SCHEME 3



SCHEME 4

This preliminary study presents evidence that the lowest singlet excited state of these chalcone oxides is (π^*, n). The dibenzoylmethanes formed are most likely derived from this state, and only one compound, *cis*-chalcone oxide, appears to be derived from a triplet state. The formation of the aldehydes observed could conceivably involve the triplet state, but the involvement of an acylcarbene similar to that observed by Griffin[20] seems certain. A substituent in the 2-position appears to exert a major effect on product formation as a result of steric and electronic factors. With the

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[19] G. W. Griffin, R. S. Becker, R. O. Bost, J. Koh, N. R. Bertoniere, and R. L. Smith, *J. Amer. Chem. Soc.*, 1970, **92**, 1302.

[20] G. W. Griffin, T. Do-Minh, and A. N. Trozzolo, *J. Amer. Chem. Soc.*, 1970, **92**, 1402; see also ref. 8.

[21] T. I. Temmikova and I. P. Stepanov, *Zhur. org. Chim.*, 1967, **3**, 2253.

exception of dibenzoylmethanes, the photoreactions of these epoxides did not give any products related to materials involved in flavonoid biosynthesis. However the dibenzoylmethanes may be involved in flavone formation, as has been shown by Kagan[5] in the photoreaction of 2′-hydroxychalcone to give 2-hydroxydibenzoylmethane, which is readily converted into flavone; hydroxyflavone and hydroxyflavanone were also obtained in that photoreaction.

[6/1057 *Received, 3rd June,* 1976]