Reactions of *m*-Chloroperbenzoic Acid with Olefins which have Neighbouring Functional Groups

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The reaction of *trans*-stilbene-2-carboxylic acid with *m*-chloroperbenzoic acid yields *trans*-3,4-dihydro-4-hydroxy-3-phenylisocoumarin. The epoxide of *trans*-stilbene-2-carboxylic acid was detected as an intermediate by n.m.r. spectroscopy. The rates of reactions of pent-4-en-1-ol and hex-5-en-1-ol with *m*-chloroperbenzoic acid are similar to that of hex-1-ene, and that of *o*-allylphenol is about twice as great as that of *o*-allylbenzene. It was concluded that these reactions also involved initial formation of an epoxide.

THE reactions of peroxy-acids with olefins which have suitably placed neighbouring functional groups frequently lead not to epoxides but to products which arise from neighbouring-group participation.[1,2] Participation could occur either at the stage at which the olefin reacts with the peracid [reaction (i)] or subsequently with attack by the neighbouring group on the epoxide [reaction (ii)]. Tinsley demonstrated that the latter occurred in the reactions of *o*-allylphenol and *o*-but-2-enylphenol with peracetic acid by isolating the epoxides and showing that they were easily converted into the coumarins.[3] We now report an investigation of the reactions of *m*-chloroperbenzoic acid with several

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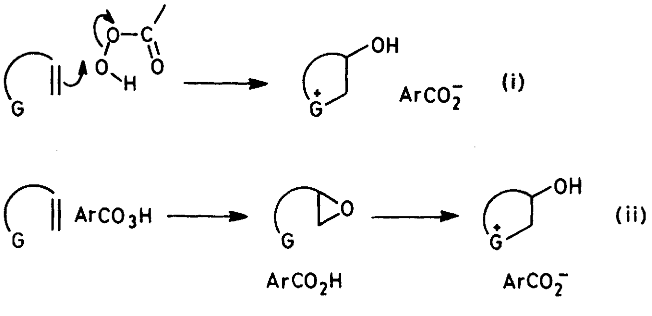
[1] *Cf.* V. I. Stanets and E. A. Shilov, *Uspekhi Khim.*, 1971, **40**, 491; *Russ. Chem. Rev.*, 1971, **40**, 272.

[2] *Cf.* D. Swern in ' Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1971, vol. 2, pp. 492—500.

[3] S. W. Tinsley, *J. Org. Chem.*, 1959, **24**, 1197; see also S. A. Harrison and D. Aelony, *ibid.*, 1962, **27**, 3311; B. Capon and J. W. Thomson, following paper.

olefins which have neighbouring functional groups. Several biosynthetic schemes involve formation of heterocycles through oxidation of olefins with neighbouring groups.[4] The mechanisms of these reactions have been discussed but no firm conclusions as to whether they proceed through epoxides are possible.



EXPERIMENTAL

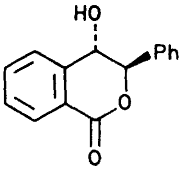
trans-Stilbene-2-carboxylic acid was prepared by the method of De Tar and Carpino and recrystallised from aqueous acid and from ethanol; m.p. 162—163° (lit.,[5] 158—160°). *trans*-Stilbene was recrystallised from ethanol; m.p. 122—123° (lit.,[6] 124°). *o*-Allylphenol, allylbenzene, hex-5-en-1-ol, pent-4-en-1-ol, and hex-1-ene were commercial samples and were purified by distillation. Commercial *m*-chloroperbenzoic acid was used without further purification and shown by titration to be 93.0% pure.

Kinetic Measurements.—Solutions in methylene chloride were used. Their peroxy-acid content was determined at suitable time intervals by withdrawing samples and adding them to solutions of potassium iodide in aqueous acetic acid. The liberated iodine was determined by titration with sodium thiosulphate (Radiometer TT1 automatic titrator and autoburette type ABU12B; platinum indicator electrode and calomel reference electrode). The second-order rate constants are given in the Table.

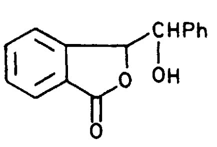
Second-order rate constants for the reactions of olefins with *m*-chloroperbenzoic acid in methylene chloride at 25 °C

	10^2k/l mol^{-1} s^{-1}
Allylbenzene	0.118
o-Allylphenol	0.235
Hex-5-en-1-ol	0.260
Hex-1-ene	0.259
Pent-4-en-1-ol	0.297
Allylurea	0.154

Reaction of trans-*Stilbene-2-carboxylic Acid with* m-*Chloroperbenzoic Acid*.—A solution of *m*-chloroperbenzoic acid (1.54 g) in methylene chloride (30 ml) was added to a solution of *trans*-stilbene-2-carboxylic acid (1.0 g) in methylene chloride (40 ml). After 24 h at room temperature t.l.c. showed that all the stilbene-2-carboxylic acid had reacted. The mixture was washed with sodium carbonate solution until the organic layer gave a negative reaction with starch–iodide paper. The methylene chloride was evaporated off until the volume was 20 ml, and light petroleum (80 ml) was added. A white crystalline solid was precipitated (0.70 g, 66%; m.p. 115—117°). The i.r. spectrum showed this to be *trans*-3,4-dihydro-4-hydroxy-3-phenylisocoumarin (1) (lit.,[7] m.p. 117—119°) [$\nu_{max.}$ 1 698s cm^{-1} but no absorption at 1 733 cm^{-1} characteristic of 3-(α-hydroxybenzyl)phthalide (2), lit.,[7] m.p. 148—149°]. The n.m.r. spectrum ($CDCl_3$) showed signals at δ 7.2—8.2 (9 H, m), 5.30 (1 H, d), 5.0 (1 H, q, H-4), and 2.5 (1 H, d, OH) (after shaking with D_2O the signal at δ 2.5 had disappeared and that at 5.0 had collapsed to a doublet). The spectrum of a reaction solution of *trans*-stilbene-2-carboxylic acid and *m*-chloroperbenzoic acid in $CDCl_3$ after 48 h [Figure (e)] showed only doublets at δ 5.0 and 5.30 characteristic of the isocoumarin (1) (with OH undergoing rapid exchange) in the region δ 0—7, so there did not appear to be an appreciable amount (<5%) of the phthalide (2) formed. Berti reported the formation of some phthalide (2) when perbenzoic acid in benzene was the epoxidizing reagent.[7]



(1)



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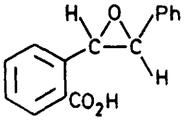

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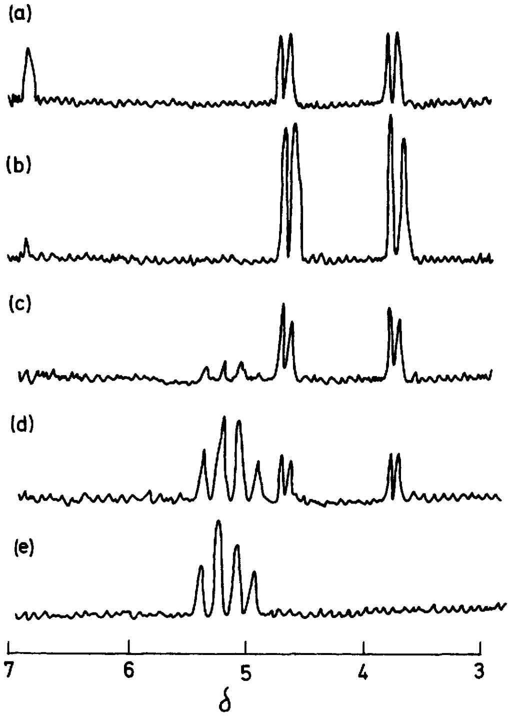

N.m.r. spectra of a reacting solution of *m*-chloroperbenzoic acid and *trans*-stilbene-2-carboxylic acid in $CDCl_3$ at *ca.* 30 °C in the range δ 3—7 after (a) 5 min, (b) 1.75 h, (c) 5.5 h, (d) 119, and (e) 149 h (the amplitude was varied from spectrum to spectrum)

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[4] R. Aneja, S. K. Mukerjee, and T. R. Seshadri, *Tetrahedron*, 1958, **4**, 256; A. D. Cross, *Quart. Rev.*, 1960, **14**, 317; E. A. Clarke and M. F. Grundon, *J. Chem. Soc.*, 1964, 4196; D. J. Austin and S. A. Brown, *Phytochemistry*, 1973, **12**, 1657; A. C. Colonna and E. G. Gros, *ibid.*, 1971, **10**, 1515.

[5] D. F. DeTar and L. A. Carpino, *J. Amer. Chem. Soc.*, 1956, **78**, 475.

[6] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, 4th edn., London, 1965, vol. 5, p. 2919.

[7] G. Berti, *J. Org. Chem.*, 1959, **24**, 934; G. Berti and F. Bottari, *Gazzetta*, 1959, **89**, 2380.

N.m.r. Spectroscopic Study of the Reaction of trans-*Stilbene-2-carboxylic Acid with* m-*Chloroperbenzoic Acid.*—The Figure (a) shows the n.m.r. spectrum in the region δ 3—7 of a mixture of *m*-chloroperbenzoic acid (0.36M) and *trans*-stilbene-2-carboxylic acid (0.22M) *ca.* 5 min after mixing. The signal at δ 6.83 is due to the vinylic protons of the stilbene-2-carboxylic acid. The doublets at δ 3.7 and 4.65 are not present in the spectra of either of the starting materials nor in the spectrum of the mixture after 48 h [Figure (e)]. After 1.75 h the signal at δ 6.83 is only just discernible and the only resonances in the region δ 0—6 are the two doublets at δ 3.7 and 4.65 [Figure (b)]. After 5.5 h two new doublets begin to appear at δ 5.0 and 5.3 and these gradually grow stronger while the signals at δ 3.7 and 4.65 grow weaker [Figures (c) and (d)] until after 48 h they are the only observed signals in the region δ 0—6 [Figure (e)].

These results show that the epoxide (3) is an intermediate in the formation of (1). The δ values of the intermediate (3.7 and 4.65) are close to those of *trans*-stilbene epoxide (4.37) [8] and the coupling constant (*ca.* 2 Hz) is characteristic of that found for unsymmetrically substituted *trans*-stilbene epoxides.[9] The doublets at δ 5.0 and 5.3 are identical with those found in the spectrum of compound (1) after the solution has been shaken with D_2O or irradiated at the frequency of the hydroxy-proton. Under the conditions of the epoxidation the hydroxy-proton undergoes rapid exchange, whereas when the isocoumarin (1) is dissolved in $CDCl_3$ alone it undergoes slow exchange.

All attempts to isolate the epoxide were unsuccessful and led only to the δ-lactone (1).

DISCUSSION

The results provide no evidence for anchimerically assisted reaction of the olefin with the peroxy-acid as in reaction (i). The rates of reactions of hex-5-en-1-ol and pent-4-en-1-ol are almost identical with that of hex-1-ene, and allylurea reacts slightly more slowly. *o*-Allylphenol reacts about twice as fast as allylbenzene, but it seems unlikely that this reaction proceeds as shown in (i) since Tinsley has isolated an intermediate epoxide in an impure state.[3] The reaction of *trans*-stilbene-2-carboxylic acid also does not occur as symbolised by reaction (i) as the epoxide (3) was detected as an intermediate (see Experimental section). This conclusion is in agreement with that of Berti and Bottari,[7] made on the basis of kinetic measurements.

Thus, in contrast to the reactions of these olefins with bromine and iodine,[1,10] there appears to be no anchimeric assistance. In fact there appears to be only one reaction of an olefin with a peroxy-acid which proceeds at an enhanced rate owing to the presence of a neighbouring group, *viz.* that of 5-*endo*-hydroxymethylnorborn-2-ene with perbenzoic acid.[11]

The mechanism by which neighbouring groups assist the reactions of olefins with halogens is uncertain.[12] It is possible that attack on the double bond by the halogen and the neighbouring group are concerted, or the halogen may react rapidly and reversibly with the double bond to form a halogenonium ion which is then attacked by the neighbouring group. Another possibility is that the neighbouring group changes the reaction from one which is thermodynamically unfavourable (*e.g.* addition of iodine under certain conditions) [13] to one which is thermodynamically favourable. By whichever way the neighbouring group causes an increase in the rate of reaction of the olefin with the halogen, and it may be different in different reactions, this way is much less effective for the reaction of an olefin with *m*-chloroperbenzoic acid. If the reaction with the halogen were a concerted process this could be rationalised by saying that this pathway is favoured because it avoids a high energy intermediate,[14] a halogenonium ion, whereas in epoxidation the intermediate is an epoxide and therefore there is less advantage to be gained by by-passing it. If the neighbouring group captures a rapid and reversibly formed halogenonium ion then on reaction with a peroxy-acid there would be no anchimeric assistance because the formation of the epoxide is irreversible. If the neighbouring group in the reaction with a halogen merely serves to convert a thermodynamically unfavourable process into a favourable one, then no effect would be expected on the rate of epoxidation, since reaction of an olefin with a peroxy-acid is normally thermodynamically favourable. Thus in general terms the difficulty in detecting an anchimerically assisted reaction of an olefin with a peroxy-acid is understandable.

[6/1981 *Received, 25th October, 1976*]

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[9] *Cf.* V. Mark, *J. Amer. Chem. Soc.*, 1963, **85**, 1884.

[10] D. L. H. Williams, E. Bienvenüe-Goetz, and J. E. Dubois, *J. Chem. Soc.* (*B*), 1969, 517; E. Bienvenüe-Goetz, J. E. Dubois, D. W. Pearson, and D. L. H. Williams, *ibid.*, 1970, 1275; S. R. Hooley and D. L. H. Williams, *J.C.S. Perkin II*, 1975, 503.

[11] H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 1959, 221.

[12] B. Capon and S. T. McManus, 'Neighboring Group Participation,' Plenum Press, New York, vol. 1, 1976, pp. 77—78.

[13] *Cf.* P. B. D. de la Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' Elsevier, Amsterdam, 1966, p. 114.

[14] *Cf.* J. E. Reimann and W. P. Jencks, *J. Amer. Chem. Soc.*, 1966, **88**, 3973; J. Hine, *ibid.*, 1972, **94**, 5766; W. P. Jencks, *Chem. Rev.*, 1972, **72**, 705.