The Photochemistry of 2,3-Bis(*p*-methoxyphenyl)oxirane: Trapping of a C–C Cleaved Intermediate in an Electron-transfer Sensitised Process

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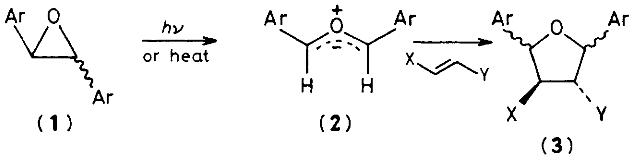
2,3-Bis(*p*-methoxyphenyl)oxirane (**6**) rearranges, with C–O cleavage, to the carbonyl compounds (**8**) and (**9**) on irradiation, direct or triplet sensitised, and thermally; in contrast C–C cleavage is observed with dicyanoanthracene as electron-transfer sensitiser, and the resulting intermediate can be trapped by dipolarophiles in synthetically useful reactions.

The generation, from oxiranes, of carbonyl ylides, and their trapping by dipolarophiles, is a well-known process, exemplified by stilbene oxides, (**1**) → (**3**). Such reactions have been studied mechanistically in detail,[1] but have not received much attention from a synthetic viewpoint; thus in reaction (**1**) → (**3**), relatively little is known about permitted variations in Ar, X, and Y. We are unaware of a natural product synthesis involving carbonyl ylides and in this context were interested in the construction of tetrahydrofuranoid lignans[2] [*e.g.* (**3**, X = Y = Me)], including the controversial 2,4-bisaryl structures, (**5a**) which were proposed for certain lignan lactones.[3] Natural products of this group contain shikimate-derived aryl rings,



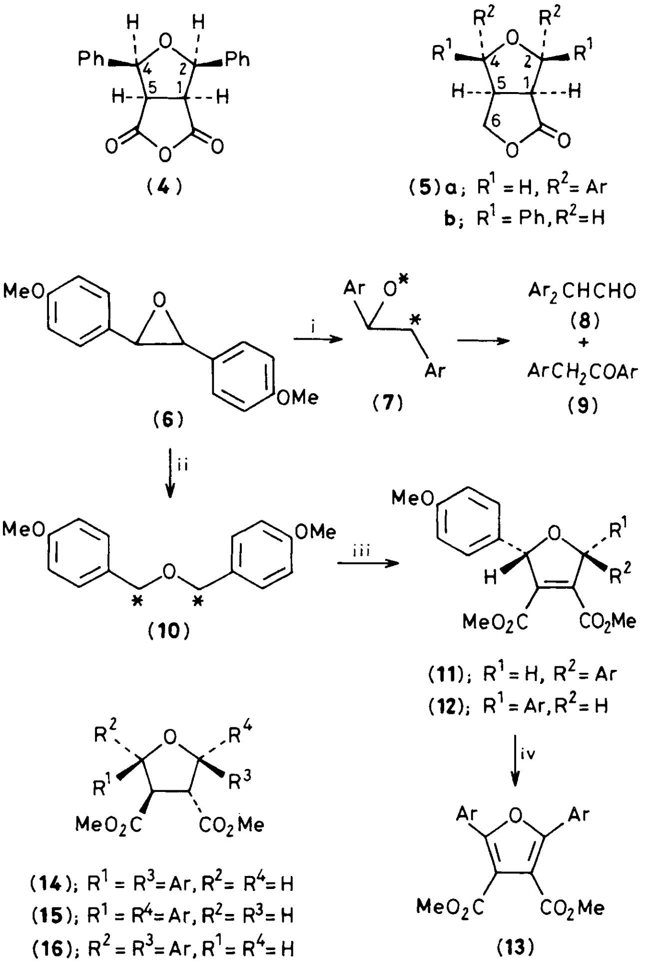
i.e. mostly bearing, at least, *para*-hydroxy or alkoxy substituents. We thus set out to investigate the key issue of the feasibility of ring opening, with C–C cleavage, in *e.g.* bis(*p*-methoxyphenyl)oxirane (**6**), to form either a carbonyl ylide *cf.* (**2**), or the isoelectronic biradical, and of the trapping of such an intermediate in useful yield. Although the methoxy groups appear to reduce aryl stabilisation in the carbonyl ylide, we felt that this might be overcome by using electron-transfer (ET) sensitisation,[4] with C–C cleavage proceeding at a cation-radical stage.

We first examined some reactions of *trans*-stilbene oxide. Direct irradiation of this epoxide in the presence of maleic anhydride is reported[5] to afford mixtures of adduct stereoisomers, none in good yield. In contrast, we observed that the same reactants on irradiation (medium pressure Hg source, Pyrex filter) in acetonitrile with 1,4-dicyanonaphthalene as ET sensitiser afforded mainly a single stereoisomer (**4**), 63%, m.p. 253 °C, with δ 3.94 (1-H, 5-H) and 5.35 (2-H, 4-H), $J_{1,2} = J_{4,5}$ = 7.4 Hz. This stereochemistry arises from *endo*-cycloaddition of the *exo,exo* conformation of the ylide. A similar reaction with but-2-enolide gave adduct (**5b**), m.p. 167—169 °C, (90%), with δ 3.5 (dd, 1-H), 3.61 (m, 5-H), 3.38 (dd, 6-H^a), 4.01 (dd, 6-H^b), 5.23 (d, 4-H), and 5.27 (d, 2-H): similar data are reported for a stereoisomer.[3d] A mixture of stereoisomers was obtained in an acetone-sensitised reaction. Addition of the ylide from *trans*-stilbene oxide, using 1,4-dicyanonaphthalene as sensitiser, also proceeded smoothly with dimethyl fumarate (63%) and dimethyl acetylenedicarboxylate (47%), the major isomer in each case arising from the *exo,exo* ylide.

The crucial question of the effect of substitution by electron donating groups was then investigated. Bis(*p*-methoxyphenyl)oxirane (**6**) and 1,4-dicyanonaphthalene were irradiated in the presence of methyl acrylate, or butenolide, but gave only a mixture, from n.m.r. examination, of the diarylacetaldehyde (**8**) and the deoxybenzoin (**9**). Such products, (**8**) and (**9**) (Ar = 3,4-methylenedioxyphenyl) were isolated, 15 and 42% respectively, from bis(3,4-methylenedioxyphenyl)oxirane under the same conditions, and also using acetone or acetophenone as triplet sensitisers. The carbonyl products clearly arise from a 1,2-hydrogen or aryl shift in a C–O cleaved intermediate (**7**). On heating these reactants at 150 °C, only traces of possible adduct could be detected.

However, prompted by the reported photo-oxidation[6] of oxirane (**6**) using 9,10-dicyanoanthracene, we investigated the use of this ET sensitiser, employing phenanthrene–toluene–Pyrex filters; reaction with dimethyl acetylenedicarboxylate proceeded cleanly, if slowly, at ambient temperature (nitrogen degassing), to afford adducts (**11**) and (**12**), (54%, 9 : 7) with heterocyclic ring protons at δ 6.08 and 6.32 ($CDCl_3$), and M^+ 398.137. Using biphenyl as cosensitiser[7] appeared to have no significant effect. Dehydrogenation of the mixture of (**11**) and (**12**) gave the crystalline furan (**13**), (60%), m.p. 92—93 °C, M^+ 396.118. Preliminary experiments indicate that a similar reaction proceeds with dimethyl fumarate, yielding the tetrahydrofurans (**14**), (**15**), and (**16**) (*ca.* 4 : 2 : 1).

These observations show that C–C cleavage of (**6**) can follow an electron-transfer process and that intermediate (**10**) can be trapped by a suitable dipolarophile. The adducts are obtained in fairly good yield and may prove useful in synthesis; *e.g.* furan (**13**, Ar = Ph) has been converted[3d] stereoselectively into lactone (**5a**, Ar = Ph).



Ar = *p*-$MeOC_6H_4$, except where otherwise stated. i, 150 °C or $h\nu$–PhCOMe, or $h\nu$–1,4-dicyanonaphthalene; ii, $h\nu$–9,10-dicyanoanthracene; iii, $MeO_2CC{\equiv}CCO_2Me$; iv, 2,3-dichloro-5,6-dicyanobenzoquinone.

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References

1 R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 572; G. W. Griffin, *ibid.*, 1971, **10**, 537; A. M. Trozzolo, T. M. Leslie, A. S. Sarpotdar, R. D. Small, G. J. Ferrandi, T. DoMinh, and R. L. Hartless, *Pure Appl. Chem.*, 1979, **51**, 261.

2 L. H. Klemm, in 'The Chemistry of Lignans,' ed. C. S. Rao, Andra University Press, 1977, p. 175.

3 (a) C. H. Brieskorn and H. Huber, *Tetrahedron Lett.*, 1976, 2221; (b) D. Lavie, E. C. Levy, A. Cohen, M. Evenari, and Y. Gutterman, *Nature*, 1974, **249**, 388; (c) R. Cooper, E. C. Levy, and D. Lavie, *J. Chem. Soc., Chem. Commun.*, 1977, 794; (d) R. Cooper, H. E. Gottlieb, D. Lavie, and E. C. Levy, *Tetrahedron*, 1979, **35**, 861; (e) A. Pelter, R. S. Ward, D. J. Watson, P. Murray-Rust, and J. Murray-Rust, *Tetrahedron Lett.*, 1978, 1509.

4 A. Albini, *Synthesis*, 1981, 249.

5 G. A. Lee, *J. Org. Chem.*, 1976, **41**, 2656.

6 S. Futamura, S. Kusunose, H. Ohta, and Y. Kamiya, *J. Chem. Soc., Chem. Commun.*, 1982, 1223.

7 A. P. Schaap, L. Lopez, and S. D. Gagnon, *J. Am. Chem. Soc.*, 1983, **105**, 663.