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THE SOLUTION PHOTOCHEMISTRY OF αβ-UNSATURATED SULPHONES [1]

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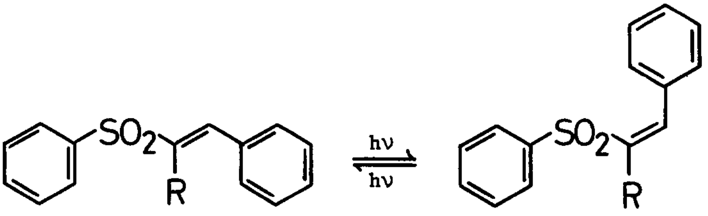
SUMMARY 1-Phenyl-2-(benzenesulphonyl)-ethylene and 1-phenyl-2-(benzenesulphonyl)-prop-1-ene have been shown to undergo Z,E-photoisomerisation, whereas 2-benzenesulphonylindene readily forms $[_{\pi}2 + _{\pi}2]$ photoadducts with 2,3-dimethylbut-2-ene, cyclopentene, and cyclohexene.

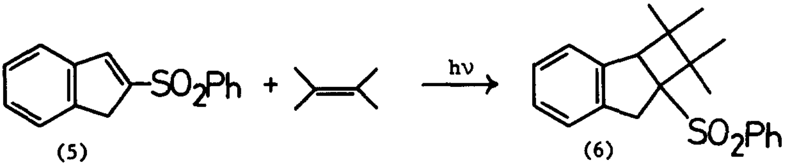
The reported failure of the acyclic αβ-unsaturated sulphones, 1-phenyl-2-(p-toluenesulphonyl)ethylene and benzenesulphonylethylene, to undergo $[_{\pi}2 + _{\pi}2]$ dimerisation is surprising in view of the ease with which αβ-unsaturated ketones, esters, nitriles and nitro-compounds react. Prolonged irradiation of these sulphones gave only black intractable oils.[2,3] In contrast, certain heterocyclic sulphones[4,5,6] are known to undergo dimerisation and $[_{\pi}2 + _{\pi}2]$ cycloaddition to alkenes. The apparent inconsistency of these observations prompted us to reinvestigate the photochemistry of αβ-unsaturated sulphones.

Irradiation[7] of E-1-phenyl-2-(benzenesulphonyl)ethylene[8] (1) in acetone solution (0.0067 mol ℓ^{-1}) was examined using ^{1}H n.m.r. spectroscopy. Signals at δ 6.86 (1H, d J = 15 Hz) and 7.70 (1H, d, J = 15 Hz), attributable to the vinyl protons, diminished in intensity on irradiation and were replaced by new signals at δ 6.52 (d, J = 12 Hz) and 7.10 (d, J = 12 Hz). These were assigned to the corresponding Z-isomer (2). Continued irradiation (4 hrs) gave a steady-state concentration of approximately 50% Z- and 50% E-isomers. No further chemical transformations were observed on prolonged irradiation or in the presence of added cyclohexene. An analogous photoisomerisation occurs with E-1-phenyl-2-(benzenesulphonyl)-prop-1-ene[9] (3) to give 70% of the Z-isomer (4); in this case, methyl signals at δ_H 2.10 and δ_C 13.10 were replaced by new signals at δ_H 2.21 and δ_C 20.74. The efficiency with which Z,E-isomerisation occurs is possibly responsible for the failure of such systems to undergo $[_{\pi}2 + _{\pi}2]$ cycloaddition reactions.



(1) R = H (3) R = Me (2) R = H (4) R = Me

Cycloaddition should, however, be favoured in cyclic sulphonylalkenes in which Z,E-isomerisation is not possible. Accordingly, we undertook a study of the photochemistry of 2-benzenesulphonylindene (5)[10] to verify this hypothesis. A solution of 2-benzenesulphonylindene (1.20 g) in a 5:1-mixture of benzene-2,3-dimethylbut-2-ene (120 ml) was irradiated until all the original sulphone had reacted as shown by t.l.c. Removal of the solvent and crystallisation of the residue from methanol gave a colourless photoproduct in 71% yield with m.p. 181-3°C; ν_{max} 1295, 1139 and 1082 cm^{-1}; δ_H ($CDCl_3$) 0.59 (3H, s), 1.08 (3H, s), 1.42 (3H, s), 1.63 (3H, s), 3.21 (1H, d, J = 19 Hz), 3.51 (1H, d, J = 19 Hz), 4.08 (1H, s) and 6.8-8.8 (9H, m); δ_C ($CDCl_3$) 21.7, 22.7, 24.3, 26.0, 38.3, 41.5, 46.0, 57.4, 73.7, 123.9, 125.2, 126.6, 126.9, 128.9, 132.9, 138.9, 141.5 and 142.5. Spectra and analytical data were in agreement with the cyclobutane structure (6). Analogous adducts were prepared with cyclohexene and cyclopentene in yields of 62 and 66% respectively.[11] Irradiation of 2-benzenesulphonylindene (1.20 g) in acetone (100 ml) under identical conditions gave a 56% yield of a high-melting insoluble photoproduct. Analytical and spectral data were consistent with a $[_\pi 2 + _\pi 2]$ dimeric structure of unknown regio- and stereochemistry; ν_{max} 1310, 1141 cm^{-1}; δ_H ($CDCl_3$) 2.38 (2H, d, J = 18 Hz), 3.30 (2H, d, J = 18 Hz), 5.19 (2H, s), and 6.3-8.1 (18H, m); δ_C ($CDCl_3$) 35.7, 51.2, 69.8, 124.7, 125.1, 127.7, 128.5, 129.4, 129.7, 134.2, 136.3, 137.2, and 144.6; m/e 540 ($M^+ < 1\%$).



2-(p-Toluenesulphonyl)- and 2-(p-chlorobenzenesulphonyl)-indenes were also prepared and converted in good yield into analogous adducts by irradiation with a variety of alkenes. In the absence of competing Z,E-photoisomerisation, therefore, $[_\pi 2 + _\pi 2]$ cycloaddition of αβ-unsaturated sulphones to alkenes can be effected.

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11. Satisfactory spectra and analytical data have been obtained for all new compounds

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