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Photochemistry of Methyl β-Styryl Sulphoxide in Protic Solvents. Polar Addition to Open Chain Olefinic Linkage

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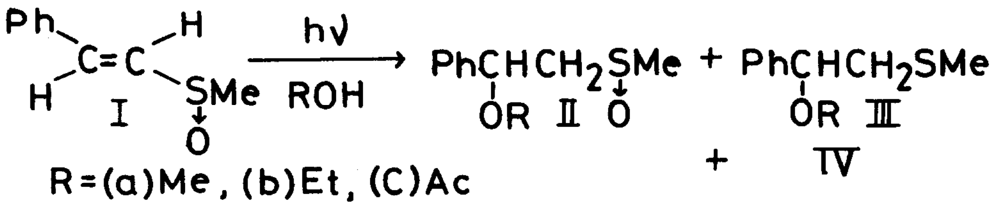
We wish to report that protic solvents are photochemically incorporated by the open chain olefinic bond of <u>trans</u>-methyl β-styryl sulphoxide[1] (I) and of <u>trans</u>-methyl β-styryl sulphide[1] (IV) in a polar fashion.

When I (λ^{MeOH}_{max} = 266 nm, log ϵ = 4.27) in a methanolic solution (150 mM) was irradiated[2] externally for 120 hr, products were isolated by preparative gas chromatography (SE30, 1 m, 140°) and identified to be β-methoxy sulphoxide IIa[1] (65%), β-methoxy sulphide IIIa[1] (8%) and vinyl sulphide IV[1] (10%) by spectral data (IR, NMR and MS), comparison with each authentic sample[1] and by chemical correlations.[3] The stereoisomerization[4] of I during the reaction was not investigated on account of the difficulty of separating the two isomers. The NMR[5] of the sulphoxide IIa indicated the presence of two diastereomers in approximately 50:50 ratio,[6] the SO-Me signals being observed at δ 2.55 and 2.60 ppm in equal intensity. Irradiation[2] of I in an ethanolic solution afforded IIb[7] (53%, bp 112-118°/0.4 mm), IIIb[7] (9%, 76-80°/0.4) and IV (9%). NMR[5] of IIb showed the formation of two diastereomers in 50:50 ratio, the SO-Me signals appearing at δ 2.55 and 2.60, -OCH$_2$CH$_3$ at δ 3.30 and 3.28 ppm both in equal intensity. A solution of I in acetic acid gave IIc[7] (60%, 126-130°/0.2) and IV (13%). NMR[5] of IIc again was indicative of the formation of two diastereomers in 50:50 ratio, the SO-Me signals at δ 2.60 and 2.63 ppm and -OCOCH$_3$ singlets at δ 2.00 and 2.05 ppm both in equal intensity. Compound IIIc was not detected. When a solution of I in each solvent was kept in the dark at room temp for 120 hr, the



starting material remained totally unchanged. The photochemistry of I in an alcoholic solution is thus in contrast to that of benzalacetone, where *trans* to *cis* isomerization and dimerization predominate.[8]

The sulphides IIa and IIb are ascribed to photoexitation of the respective vinyl sulphides IV. Irradiation[2] of *trans* vinyl sulphide IV ($\lambda_{max}^{MeOH} = 286$ nm, log $\epsilon = 4.51$) in a methanolic or an ethanolic solution for 48 hr afforded the corresponding sulphide IIIa and IIIb in 15% and 8% yield, respectively. Isomerization to the *cis* sulphide was observed, t/c ratio being 1:2. The sulphides IIIa and IIIb were not obtained either on standing the alcoholic solution of IV in the dark or on irradiation[2] of the sulphoxide IIa and IIb. Reduction of I to IV has been observed in aprotic solvents. Irradiation[2] of I (3 mmoles) in a mixture of THF (10 ml) and cyclohexane (10 ml) for 72 hr gave the sulphide IV in 18% yield.

The photoaddition of trialkylboranes to various kinds of C=C bonds has been recorded.[9] Remarkably, the reaction of I with boranes proceeded at room temp under nitrogen in the dark. Standing an equimolar mixture of I and tri-*n*-butylborane in THF for 48 hr at room temp and work up of the reaction mixture with alkaline hydrogen peroxide gave *trans*-1-phenyl-1-hexene Vd[10] (55%) along with IV (5%). GLC analysis indicated that no trace of the *cis* isomer of Vd was formed. Similarly, I reacted with triisopropylborane under the analogous conditions to afford *trans*-3-methyl-1-phenyl-1-butene Ve[10] (63%) along with IV (3%).

REFERECES AND REMARKS

(1) G. A. Russel, E. Sabourin and G. J. Mikol, *J. Org. Chem.*, **31**, 2054 (1966). (2) All photolyses were carried out in a Pyrex tube at room temp under nitrogen using an external 200 W high pressure mercury arc. (3) LAH reduction of IIa and IIb in THF gave IIIa and IIIb respectively. (4) The stereoisomerization of 1-methylsulfinyl-1-methylthio-2-phenylethylene in methanol on irradiation was reported by K. Ogura and G. Tsuchihashi, *Tetrahedron Lett.*, 1383 (1972). (5) NMR spectra were obtained in $CDCl_3$ with TMS. (6) Base (NaOMe, Triton B)-catalysed thermal addition of alcohols to vinyl sulphoxide was reported by (a) J. R. Alexander and H. McCombie, *J. Chem. Soc.*, 1913 (1931), (b) M. Schostakovski, E. N. Prilezhaeva, L. V. Tsymbal, R. Ya, Tolchinskaya and N. G. Starova, *Zhur. Obshchei Khim.*, **31**, 2496 (1961). (7) All new compounds gave correct elemental analyses. (8) A. Butenandt, L. Karlson-Poschmann, G. Failer, U. Schied and E. Biekert, *Ann.*, **575**, 123 (1952); H. O. House, *J. Org. Chem.*, **23**, 1374 (1959). (9) N. Miyamoto, S. Isiyama, K. Utimoto and H. Nozaki, *Tetrahedron Lett.*, 4597 (1971). (10) M. Schlosser and K. F. Christmann, *Angew. Chem. Intern. Ed.*, **5**, 126 (1966).