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Novel Photooxidation of Organic Sulphides to Sulphoxides Sensitized by 1,4-Dimethoxynaphthalene

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Abstract : Efficient and selective photooxidation of organic sulphides to sulphoxides under 1,4-dimethoxynaphthalene sensitization is described.

Photooxidation of organic sulphides has received extensive study under a variety of reaction conditions, viz. i) autooxidation,[1-3] ii) electron transfer sensitization (eg. 9,10-dicyanoanthracene[4] and TiO_2[5]) and iii) singlet oxygen oxidation.[6,7] Organic sulphides exhibit weak absorption in the longer wavelength region in oxygenated solvents due to charge transfer interaction with molecular oxygen and under direct photostimulation they undergo autooxidation and convert essentially to sulphoxides. However, tert-butylsulphide does not undergo autooxidation though it exhibits intense absorption due to charge transfer interaction with molecular oxygen.[1] Direct IR evidence obtained by Akasaka et al.[3] in the charge transfer photooxidation of sulphides under cryogenic oxygen matrix confirms the involvement of a persulphoxide zwitterion as the reactive intermediate. Although a similar charge transfer mechanism is believed to be involved under cyanoaromatic and semiconductor sensitizations, they produce both sulphoxide and sulphone in nearly equal proportion. As a part of our ongoing study on electron rich arene sensitized oxidative organic transformations,[8] we have recently observed 1,4-dimethoxynaphthalene[9] (DMN) to sensitize efficient and selective photooxidation of sulphides 1-6 to the corresponding sulphoxides through an electron transfer mechanism. This process (equation 1) is represented with the results of each compound (irradiation hours, yield) :

$$R^1SR^2 \xrightarrow[O_2,\ CH_3CN]{h\nu,\ DMN} R^1SOR^2 \qquad (1)$$

1 $R^1 = R^2 = Bu^t$ (4h, 89%); 2 $R^1 = R^2 = Ph$ (6h, 98%); 3 $R^1 = Ph$, $R^2 = Me$ (4h, 93%);

4 $R^1 = R^2 = PhCH_2$ (4h, 90%); 5 $R^1 = Ph$, $R^2 = CH_2\text{-}CH=CH_2$ (4h, 92%); 6 $R^1 = R^2 = Bu^n$ (3h, 86%).

In a typical procedure, tert-butylsulphide, 1 (1.5 g, 10.3 mmol) and DMN (0.94 g, 5 mmol) were taken in 250 ml of oxygenated acetonitrile and irradiated for 4 h using fluorescent lamps having maximal emission at 350 nm. Progress of the reaction was followed by glc using SE-30 column. After completion of the reaction, solvent was removed under reduced pressure and the sulphoxide (1.48 g, 89%) was separated from the reaction mixture by normal column chromatography. The isolated product was characterized by ^1H NMR, Mass and IR spectral data.

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In control experiments, when sulphides 1-6[10] were irradiated directly using identical fluorescent lamps in oxygenated acetonitrile, sulphides 3-6 showed less than 10 per cent conversion and sulphides 1 and 2 did not react after 12 h of irradiation. But under DMN sensitzation, sulphides 1-6 converted to sulphoxides in good yields (> 85%) in less than 6 h. Phenylsulphide, 2 reacts very efficiently under DMN sensitization, however, it is inert towards singlet oxygen.[6,11] Thus it appears that singlet oxygen is not involved (at least as major path) under the reaction conditions.

Photooxidation of sulphides under DMN sensitization is found to be efficient in polar solvents like acetonitrile and methanol but in nonpolar solvents like cyclohexane, no appreciable reaction is observed. As it could be understood from the photocyanation experiments of Pac et al.[12] that photoexcited methoxynaphthalenes readily from arene radical cations in polar solvents by electron transfer to molecular oxygen, we also believe that the oxidation of sulphides to sulphoxides under DMN sensitization is initiated by DMN radical cations generated under the reaction conditions :

$$\mathrm{DMN} \xrightarrow{h\nu} \mathrm{DMN}^{*} \xrightarrow[\text{polar solvent}]{O_2} \mathrm{DMN}^{+\cdot} + O_2^{-\cdot}$$

$$\mathrm{DMN}^{+\cdot} + R_2S \longrightarrow \mathrm{DMN} + R_2S^{+\cdot}$$

$$R_2S^{+\cdot} + O_2^{-\cdot} \longrightarrow [R_2S^{+}\text{-}O\text{-}O^{-} \longleftrightarrow R_2S{=}O^{+}\text{-}O^{-}] \xrightarrow{R_2S} 2R_2SO$$

In conclusion, this work describes a mild and selective photochemical approach for oxidation of sulphides to sulphoxides and is the first description of photooxidation of organic sulphides under electron rich arene sensitization. Application of this method in the preparation of sulphoxide intermediates of pharmaceutical compounds like 6-Aminopenicillanic acid, Omeprazole, Timoprazole and Sulmazole is under study.

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