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Novel Photooxidation of Alkenes Sensitized by p-Dimethoxybenzene[1]

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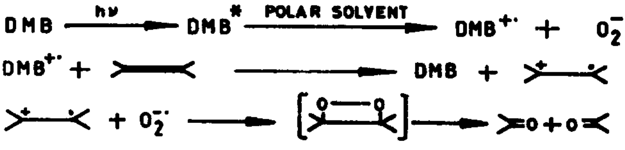
Abstract : Photoexcited p-dimethoxybenzene catalyses oxidative cleavage of various alkenes to corresponding carbonyls in the presence of oxygen.

Like inorganic semiconductors, several aromatic compounds having electron donating groups also exhibit photoinduced electron transfer to molecular oxygen[2] as well as electron ejection[3] in polar solvents forming arene radical cations (equivalent to holes generated on irradiated semi-conductor surface). Based on this phenomenon semiconductors are extensively studied as sensitizers in carrying out various oxidative conversions[4], but the studies on the scope for similar sensitizer activity of electron rich arenes is still awaited. We initiated studies in this direction and recently identified various methoxylated benzenes having low lying excited states (>280 nm) which initiate photooxidation of amines to amine radical cations by electron transfer[5]. This interesting observation lead us further to study the possibility of carrying out various oxidative conversions under homogeneous conditions replacing inorganic semiconductors. Here we wish to report the novel photooxidation of alkenes to carbonyls sensitized by p-dimethoxybenzene (DMB). The representative results are given in Table I.

In a general procedure, alkene and DMB[6] (1 mmol each) are taken in 500 ml of acetonitrile and irradiated at room temperature with medium pressure 450W Hanovia mercury arc lamp using a pyrex sleeve (> 280 nm) for 12h under an oxygen atmosphere. Progress of the reaction is followed by glc using SE-30 column and the products were isolated by normal column chromatography and compared with authentic samples.

In the absence of DMB and in deaerated polar solvents alkenes are not oxidized. We find this reaction to proceed efficiently in polar solvents like acetonitrile but nonpolar solvents could not promote the reaction. Carbonyls are the only oxidation products observed under DMB sensitization and we expect their formation from the corresponding dioxetanes formed by olefin radical cations reacting with super oxide anion ($O_2^{-\cdot}$). We could not identify the formation of dioxetanes during irradiation possibly because they readily cleave to carbonyls in polar solvents.[7]

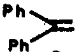
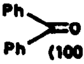
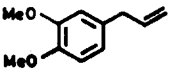
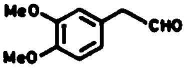
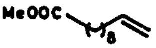
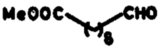
To look for the possibility of singlet oxygen as oxidant we irradiated tetramethylethylene which reacts efficiently with singlet oxygen forming 'ene' product as major component (85%)[8], but we could not observe formation of the ene product. Stilbene (4) is inert towards singlet



Scheme 1

oxygen[9] but when irradiated in presence of DMB it cleaved to benzaldehyde. These observations tentatively suggest the involvement of a non-singlet oxygen mechanism, possibly electron transfer (Scheme 1) as the major path for the observed oxidation of alkenes.

Table I : p-Dimethoxybenzene Sensitized Photooxidation Alkenes[a].

Alkene	% Conversion	Products (chemical yields)[b]
 1	90	 (100)
 2	80	 (100)
 3	60	Ph-CHO (30)[c]
 4	90	Ph-CHO +  (60)[d] (40)
 5[e]	30	 (100)
 6	30	 (100)

a) Acetonitrile is used as solvent; irradiation time 12 h; b) Yields are based on the recovered starting material; c) Oligomeric products accounted for the remainer of consumed starting material; d) Yield is based on the expected formation of 2 moles of benzaldehyde from each mole of stilbene; e) Self-sensitizer.

In conclusion, this work offers a mild method for oxidative cleavage of alkenes and is the first observation of reaction under an electron rich arene sensitization. Further work extending the scope and mechanistic evaluation of DMB sensitization is in progress.

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