Methoxylated Benzene Sensitized Photoformylation of Aliphatic Primary and Secondary Amines†

U. T. Bhalerao* and M. Sridhar

Organic Division II, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Methoxylated benzene derivatives catalyse photooxidation of aliphatic primary and secondary amines to their *N*-formyl derivatives.

Although semiconductors like TiO_2 and CdS are available as electron-transfer sensitizers to effect photooxidation of aliphatic amines[1] and olefins,[2] no organic counterpart is known to simulate similar oxidations. As aromatic compounds with electron donating substituents exhibit photoinduced electron transfer to molecular oxygen[3] as well as electron ejection in polar solvents forming arene radical cations,[4] we envisaged that instead of using semiconductors, these photogenerated arene radical cations could be directed to oxidize suitable electron donors with relatively lower oxidation potential. We have realized this by oxidizing aliphatic primary and secondary amines with photoexcited methoxylated benzenes (MBs).

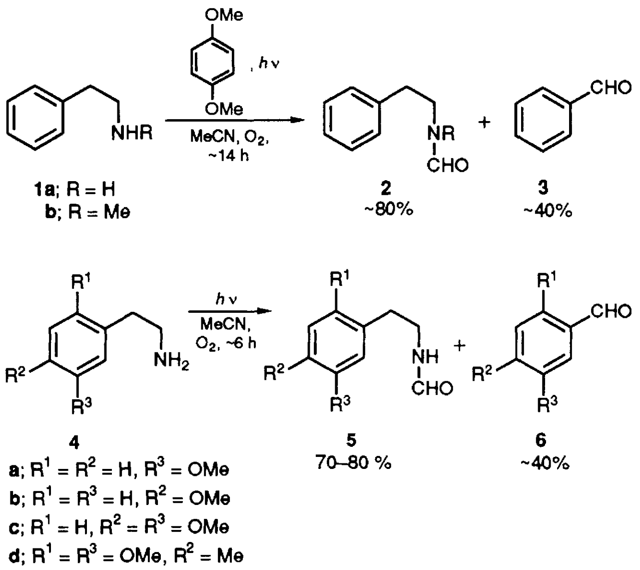
Our preliminary studies with various MBs having low lying excited states (>280 nm)‡ show that these compounds can efficiently catalyse photooxidation of aliphatic primary and secondary amines. These MBs were recovered as such (>90%) after completion of reaction and in their absence no reaction is observed with **1a** and **b** even after 24 h irradiation. The amines, **1a** and **b** and **4a–d** upon irradiation in the presence of *p*-dimethoxybenzene formed their corresponding *N*-formyl derivatives, **2a** and **b** and **5a–d** along with the benzaldehydes **3** and **6a–d**, respectively§ (Scheme 1). **4a–d**

---

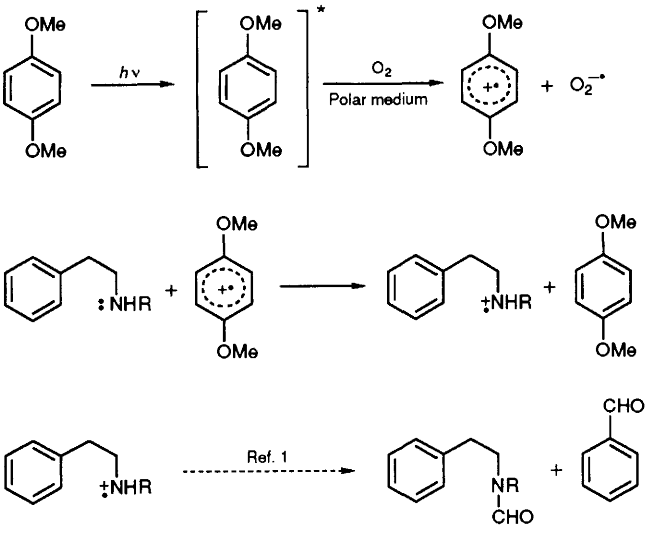
† IICT Communication No. 3103.

‡ Anisole, varatrole, 4-methoxytoluene, 1,4-dimethoxybenzene, 1,5-dimethoxytoluene and 1,3-dimethoxytoluene were all found to catalyse photooxidation.

§ General procedure used for MB catalysed photooxidation of aliphatic primary and secondary amines is as follows: phenethylamine **1a** (2 g, 16.5 mmol) and 1,4-dimethoxybenzene (1 g, 7.2 mmol) were irradiated for 14 h with a medium pressure Hanovia mercury lamp (450 W) using a Pyrex sleeve (λ > 280 nm) in 500 ml of acetonitrile saturated with oxygen. Progress of the reaction was followed by gas-liquid chromatography using OV-17 column which showed the formation of three major products. After completion of the reaction, solvent was removed and two of them **2a** (0.99 g, 80%) and **3a** (0.35 g, 40%) were isolated using normal chromatography. The third one was identified by GLC–mass spectral analysis of the reaction mixture to be the Schiff base formed by the benzaldehyde, **3** with its precursor amine **1a**. The yield of **2a** is calculated based on expected consumption of 2 mol of reactant for each mol of formylation product. Satisfactory IR, mass, ^1H NMR spectral data were obtained for the products.



Scheme 1



Scheme 2

reacted by self-sensitization and with enhanced rates which could possibly be due to more competitive intramolecular electron transfer. In deaerated polar solvents as well as in moisture-free nonpolar solvents photooxidation did not proceed. We believe¶ that the mechanism given in Scheme 2 is operative in generating the aminium radical cation which in the presence of oxygen leads to the formation of the observed products.[1]

In conclusion, this work is the first description of photooxidation of aliphatic primary and secondary amines under homogeneous conditions. It identifies a new facet of methoxylated benzene as electron transfer sensitizer. As the MB unit is present in several natural products, evaluation of its role in their plausible photooxidation conversions is in progress.

Received, 1st September 1992; Com. 2/04671G

References

1 M. A. Fox and C. C. Chen, *J. Am. Chem. Soc.*, 1983, **105**, 4497; M. A. Fox, *Acc. Chem. Rec.*, 1983, **16**, 314.

2 T. Kanno, T. Oguchi, H. Sakaragi and K. Tokumaru, *Tetrahedron Lett.*, 1980, **21**, 467; M. A. Fox and C. C. Chen, *J. Am. Chem. Soc.*, 1981, **103**, 6757; M. A. Fox and J. N. Younathan, *Tetrahedron*, 1986, **42**, 6285.

3 R. Potashnik, C. R. Goldshmit and M. Ottolenghi, *Chem. Phys. Lett.*, 1971, **9**, 424; Y. Taniguchi, A. Mioshi, N. Mataga, H. Shizuka and T. Morita, *Chem. Phys. Lett.*, 1972, **15**, 2223; J. Den Heijer, O. B. Shadid, J. Cornelisse and E. Havinga, *Tetrahedron*, 1977, **33**, 779; M. Yasuda, C. Pac and H. Sukurai, *J. Chem. Soc. Perkin Trans. 1*, 1980, 746.

4 L. I. Grossweiner, G. W. Swenson and E. F. Zwicker, *Science*, 1963, **141**, 805; J. Jortner, M. Ottolenghi and G. Stein, *J. Am. Chem. Soc.*, 1963, **58**, 2712; G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.*, 1965, **61**, 708; H. I. Joschek and L. I. Grossweiner, *J. Am. Chem. Soc.*, 1966, **88**, 3261; J. Zechner, G. Kohler, G. Grabner and N. Getoff, *Chem. Phys. Lett.*, 1976, **27**, 292; G. Grabner, W. Rauscher, J. Zechner and N. Getoff, *J. Chem. Soc., Chem. Commun.*, 1980, 222.

¶ We could not detect phenylacetaldehyde in the reaction mixture although its formation as an intermediate is evident from the formation of the observed products. Possibly due to the rapid condensation of phenylacetaldehyde with amine under the experimental conditions.