The Photochemical Oxidation Reaction of Benzylic Alcohols in Dimethyl Sulfoxide

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Of the numerous reactions using dimethyl sulfoxide (DMSO), the oxidation reaction of alcohols to aldehydes and ketones has been reported from several laboratories.[1-3] This paper will record a new approach, the use of DMSO as a solvent for the photochemical oxidation reaction of benzylic alcohols under neutral conditions at room temperature.

On irradiation,[4] a solution of 9-hydroxyfluorene in DMSO absorbed oxygen smoothly, and after 9 hr. 9-fluorenone was isolated in a 71% yield (conversion). 1-Phenylethanol was also converted to acetophenone in a 53% yield (as 2, 4-dinitrophenylhydrazone), whereas benzhydrol afforded 61.5% of benzophenone, together with 21% of bis(diphenylmethyl) ether.[5]

Since this oxidation reaction seemed to be rather general, several varieties of benzyl alcohols were also subjected to the reaction conditions in the hope of obtaining the corresponding aldehydes. A mixture of benzyl alcohol (0.5 mol.) and DMSO (2.5 mol.) absorbed 0.27 mol. of oxygen during 13.5 hr. to form 38% of benzaldehyde (as 2, 4-dinitrophenylhydrazone), the yield of benzoic acid being 13.6%. In one experiment, in which a 1 : 2 solution of benzyl alcohol and DMSO was used, the reaction mixture was analyzed by the vapor phase chromatography of the aliquots removed at one-hour intervals for over 20 hr. using 30% Carbowax-1500 on a celite column at 190°C.[6] It was found that the yield of benzaldehyde reached a maximum (48%) in 14 hr. It was well established that the otherwise very slow uptake of oxygen was much facilitated by the use of DMSO as a solvent. Although the formation of a small amount of dimethyl sulfone was shown to accompany this reaction, the rest of the DMSO could be recovered by distillation. Other solvents, including dimethylformamide, acetonitrile and ligroin, were shown to be not effective. The fact that the aldehyde group was protected in DMSO from further oxidation into the carboxyl group was confirmed by comparing the irradiation reaction of benzaldehyde in DMSO and in other solvents, for example ligroin, in which photo-oxygenation occurred quite rapidly. In the DMSO solution 83.7% of benzaldehyde could be recovered, even after irradiation for 9 hr. under vigorous shaking in oxygen.

p-Methyl- and *p*-methoxybenzyl alcohols gave the corresponding benzaldehydes in 46.5 and 37.5% yields respectively, the uptake of oxygen being much faster in these compounds than in benzyl alcohol. *m*-Methyl- and *p*-isopropylbenzaldehydes (35.1 and 37.7% yields respectively) were also prepared by this method. On the other hand, *p*-chloro-, *m*- and *p*-nitrobenzyl alcohols were recovered unchanged. *p*-Bromobenzyl alcohol, however, gave 15% of the aldehyde upon irradiation in a quartz vessel.

Finally, mention should be made of the photochemical stability of sulfoxides. DMSO itself resisted the photochemical oxygenation reacion, and only 1.4% of dimethyl sulfone was formed after 12.5 hr. In a quartz vessel it was irradiated for 20.5 hr. under nitrogen to give a small amount of dimethyl sulfide and dimethyl sulfone (both less than 1%), 92% of DMSO being recovered.[7] Likewise, diphenyl sulfoxide was found to be quite stable toward benzene light. In contrast, a benzene solution of dibenzyl sulfoxide, when irradiated under nitrogen in a quartz cell, was shown to be decomposed into benzyl mercaptan (isolated as dibenzyl disulfide) and benzaldehyde.

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[1] K. E. Pfitzner and J. G. Moffat, *J. Am. Chem. Soc.*, **85**, 3027 (1963).

[2] V. J. Traynelis and W. L. Hergenrother, ibid., **86**, 298 (1964).

[3] T. Sato, A. Takatsu and K. Hata, This Bulletin, **37**, 902 (1964), and the literature cited therein.

[4] Unless otherwise stated, in all the photochemical reactions described here a solution of alcohol and DMSO (1 : 5) was placed in a Pyrex vessel connected with a buret for the measurement of the oxygen uptake; then, under vigorous shaking, it was irradiated with a 1000 W. mercury arc lamp (Wako Denki Co., HBC-1000) mounted in a water-cooled Pyrex jacket. The yield is based on the starting materials used, except for 9-fluorenone.

[5] The irradiation of benzhydrol in a quartz cell led to the formation of benzopinacol.

[6] V. E. Cates and C. E. Meloan, *Anal. Chem.*, **35**, 658 (1963).

[7] Cf. G. O. Schenk and C. H. Krauch, *Chem. Ber.*, **96**, 517 (1963).