Photooxidation with Cupric Ions. A Novel Dimethoxylation and Diacetoxylation of Styrene

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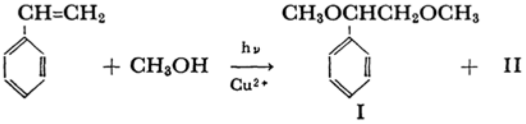
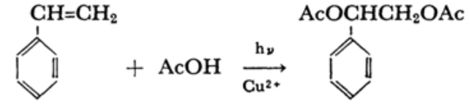
Previous investigations of photooxidation with transition metal ions have dealt almost exclusively with aqeuous solutions.[1] The hydroxylation of benzene[2] and benzoic acid[3,4] to the corresponding phenols by irradiation with ultraviolet light in an aqeuous ferric ion solution have been reported. Recently Kochi has reported the photochemical chlorination of organic compounds in organic media.[5]

We wish now to report some novel photooxidations in nonaqeuous solutions: the photochemical reactions of styrene with methanol or with acetic acid in the presence of cupric ions. The over-all reactions are shown below:



I

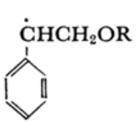


III

A homogeneous solution of styrene (0.1 mol.) and cupric perchlorate hexahydrate (0.1 mol.) in methanol (200 mol.) was irradiated by 2537Å light for 24 hr. The reaction mixture was then diluted with water and extracted with ether.[6] The ether extract was dried and distilled to give 2.4 g. of styrene glycol dimethyl ether (I), b. p. 90—95°C/11 mmHg, and 1.7 g. of an almost colorless oil, b. p. 110—120°C/0.5 mmHg, which was partially crystallized on standing and which was separated by filtration into 0.2 g. of crystalline *meso*-1, 4-dimethoxy-2, 3-diphenylbutane (II) and an oil. This oil, obtained also in the absence of cupric perchlorate, was presumably a mixture of styrene dimers (infrared). When compound I was purified by preparative gas chromatography, it showed an infrared spectrum identical with that of an authentic sample.[7] Found: C, 72.29; H, 8.77. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%. II was recrystallyzed from methanol, m. p. 129—130°C, underpessed on admixture with an authentic sample.[7] When the reaction of styrene with methanol was carried out, under irradiation, using cupric sulfate pentahydrate in place of cupric perchlorate, I (0.3 g.) and II (0.2 g.) were also obtained.

In the same manner, a homogeneous solution of styrene (0.1 mol.) and cupric perchlorate hexahydrate (0.1 mo.l) in acetic acid (400 ml.) was irradiated by 2537Å light for 24 hr. No gas evolution was observed during the reaction. On working up as has been described above, 1.5 g. of styrene diacetate (III), b. p. 102—105°C/0.3 mmHg was obtained. III was identified by gas chromatography on a polyester-DA column at 185°C. III also showed an infrared spectrum identical with that of an authentic sample.[8] III gave styrene glycol upon hydrolysis, m. p. and m. m. p. 65—66°C (ligroin).

Upon irradiation in the absence of styrene, a solution of cupric perchlorate in methanol gave formaldehyde, while in acetic acid the products were mainly CH_4 and CO_2, with small amounts of H_2 and C_2H_6. Therefore, in these reactions the methoxy radical or the acetoxy radical are probably formed initially by the photooxidation of methanol or acetic acid with cupric ions. Then addition of these radicals to styrene probably takes place, thus yielding intermediate radicals such as IV.



IV $R=CH_3$, Ac

Finally, IV gives I or III by the usual cupric ion oxidation of free radicals.[9] Small amounts of fine precipitates of metallic copper were obtained throughout these reactions. Cupric ions might be reduced to cuprous ions, which might then disproportionate to cupric ions and metallic copper. However, the possibility of the initial formation of the styrene cation radical by a photochemical one-electron oxidation of styrene with cupric ions and the trapping of the cation radical by solvents, thus yielding IV, has not been eliminated.

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1) N. Uri, *Chem. Revs.*, **50**, 375 (1952).

2) J. H. Baxendale and J. Magee, *Trans. Faraday Soc.*, **51**, 205 (1955).

3) H. G. C. Bates and N. Uri, *J. Am. Chem. Soc.*, **75**, 2754 (1953).

4) J. Saldick and A. O. Allen, ibid., **77**, 1388 (1955).

5) J. K. Kochi, ibid., **84**, 2121 (1962).

6) *Caution;* Avoid concentrating the reaction mixture or serious explosion would take place.

7) T. Inoue and S. Tsutsumi, This Bulletein, **38**, 661 (1965).

8) W. L. Evans and L. H. Morgan, *J. Am. Chem. Soc.*, **35**, 54 (1913).

9) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).