A New Solvent System for Photo-oxidations

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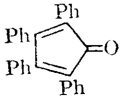
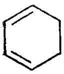
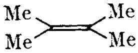
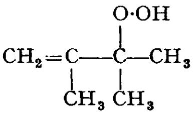
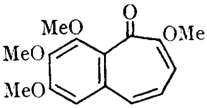
PEROXIDATIONS of organic compounds in the liquid phase may often be effected by light in the presence of a sensitizer. Occasionally a substance may act as its own sensitizer, and in such cases Dufraisse has shown that carbon disulphide is easily the most efficacious solvent.[1] In our experience however self-sensitized reactions lead to more complex reaction mixtures than those in which an added sensitizer, such as Rose Bengal or hæmatoporphyrin dihydrochloride, is used. These sensitizers have not been used in carbon disulphide on account of their insolubility. We have been able to combine the beneficial effects of the sensitizer and carbon disulphide in a new solvent system comprising a mixture of carbon disulphide, methanol (or ethanol), and ether (*ca.* 14 : 1 : 1·5 v/v). Thus the rates of photo-oxidations of tropones[2] and benztropones[3] are greatly enhanced in this solvent system as compared with methanol alone as the solvent. It has now been shown that this new solvent system is of general application to photo-oxidations of aliphatic dienes and to appropriate mono-enes using two of the most useful sensitizers. For comparison the reaction of an aromatic system is listed.

yields are often better or at least comparable with those obtained in other solvents. Particularly notable however is the greatly enhanced rate of reaction. If the function of the sensitizer is to produce singlet oxygen,[7] and there is much evidence to support this view,[8] then the role of the carbon disulphide is probably that of an efficient promotor of singlet–triplet intersystem crossing. In this way a higher concentration of triplet sensitizer is built up and singlet oxygen is thereby produced the more readily. It is notable that in this new solvent system the fluorescence of the sensitizer is markedly reduced. It has been noted previously that the self-sensitized photo-oxidation of anthracene proceeds faster in non-fluorescent solutions.[9]

TABLE

	Sensitizer Solvent	Time (hr.) (% Yield)[a]	Time (hr.) (% Yield)[b]	Product
	Methylene Blue CH_2Cl_2/C_6H_6[4]	8 hr. 65%	1·5 hr. 67%	*cis*-Dibenzoylstilbene
	Methylene Blue Isopropanol[5]	4·2 13	2·3 36	*endo*-Peroxide
	Rose Bengal Methanol[6]	4 82	1·5 75	 $CH_2{=}C(CH_3){-}C(O{\cdot}OH)(CH_3){-}CH_3$
	Rose Bengal Methanol[3]	28 22	5 43	A γ-lactone

[a] and [b] are relative time and yields of experiments reported in the literature for the solvent quoted and the new solvent system, respectively.

In a typical experiment, a solution of the olefin (0·5 g.) in solvent (80 ml.) was irradiated with a 300 w tungsten filament lamp at room temperature. To obtain comparative results we have repeated earlier experiments using the same sensitizers and solvents as previously used but with the tungsten filament light source.* In all cases yields quoted are for pure isolated material.

It can be seen that with the new solvent system

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* Many photo-oxidations using sensitizers which absorb in the visible region of the spectrum have been effected with mercury arc sources, *e.g.*, ref. 5 and 6.

[1] C. Dufraisse, *Compt. rend.*, 1935, **200**, 1103.
[2] E. J. Forbes and J. Griffiths, *Chem. Comm.*, 1966, 896.
[3] E. J. Forbes and J. Griffiths, *J. Chem. Soc.* (*C*), 1967, 601.
[4] C. F. Wilcox and M. P. Stevens, *J. Amer. Chem. Soc.*, 1962, **84**, 1258.
[5] G. O. Schenck and K. Ziegler, Ger. Pat. 913,892 (*Chem Abs.*, 1958, **52**, 14704).
[6] G. O. Schenck and K. H. Schulte-Elte, *Annalen*, 1958, **618**, 185.
[7] H. Kautsky, *Trans. Faraday Soc.*, 1939, **35**, 216.
[8] C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, 1964, **86**, 3879.
[9] E. J. Bowen, *Discuss. Faraday Soc.*, 1953, **14**, 143.