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ISOTOPIC TESTING OF A MECHANISTIC POINT IN PHOTOSENSITIZED EPOXIDATION

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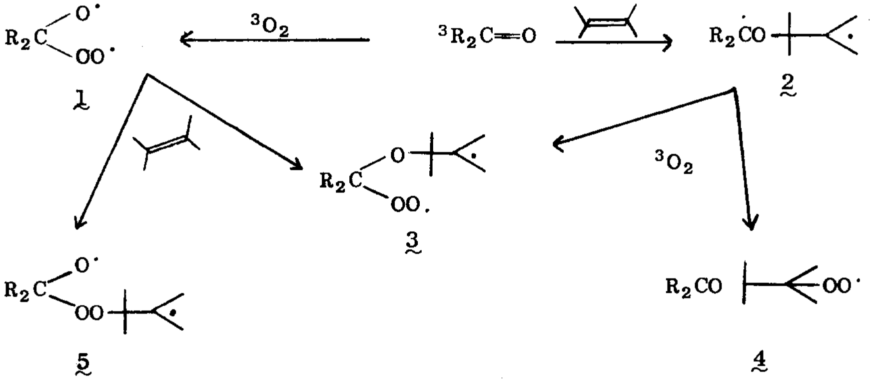
Since 1974, many cases have been reported in which photo-epoxidation competes with the usual reactions of singlet oxygen,[1] influenced by the nature and concentration of the sensitizer[2], the solvent[1,2,3], substrate[3], additives[2], and wavelength of light used.[2] The cleanest photosensitized epoxidation occurs with α-diketones[4], which often lead to high yields of epoxide with no sign of the production of singlet oxygen, but with substantial attendant destruction of the sensitizer.

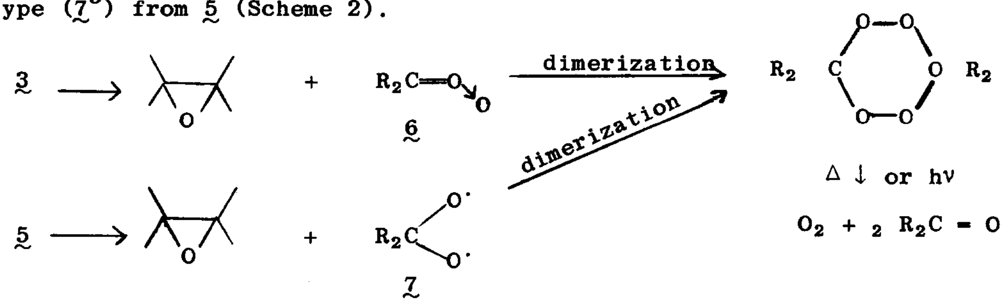
In speculating on the mechanism of photosensitized epoxidation, it was reasonable to begin with the possible biradical-forming reactions between triplet excited ketone and either triplet oxygen or ground-state olefin.

Scheme 1 shows several such possibilities, according to whether the ketone (of which only one carbonyl group is shown, for simplicity) reacts first with oxygen or with olefin, involving termolecular intermediate 3, 4, or 5. By scheme 2, epoxide formation through 3 would lead to product whose epoxy oxygen was that of the sensitizer carbonyl and to regenerated ketone (via fragmentation of carbonyl oxide dimer) containing an atom from the original molecular oxygen. Intermediaey of 5, on the other hand, would lead to epoxide oxygen stemming entirely from the



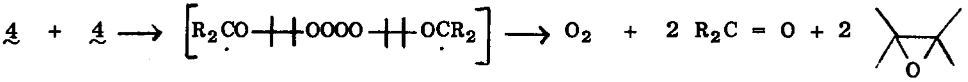
Scheme 1.

O_2 and a symmetrical carbonyl oxide 7[5] which must lead to 50% oxygen exchange in the regenerated ketone. Species 3 and 5 could each fragment to epoxide and a carbonyl oxide, of the unsymmetrical Criegee type (6) from 3 and of the symmetrical type (7[5]) from 5 (Scheme 2).



Scheme 2.

In addition there are analogies[6] for a peroxy-biradical such as 4 undergoing a bimolecular process like the normal termination reaction in autoxidation chains (Scheme 3)[7].



Scheme 3.

From labeled molecular oxygen and a monoketone sensitizer, these three processes should lead to epoxide and recovered ketone labeled as shown in Table I.

Table I. % Labeling of Products from $^*O_2$

via Intermediate	Epoxide	Recovered Ketone after one cycle
3	0	100%
4	100%	0
5	100%	50%

With benzil or biacetyl the recovered ketone would show half this amount of isotopic labeling per molecule, if only one C=O is involved.

Table II shows the results of 15-minute irradiations, with a Hanovia 450-W mercury lamp, of benzene solutions of 0.20 mmol each of norbornene and either benzil or biacetyl, with 0.36 mmol of 99.9% $^{36}O_2$, the products being analyzed by GC-mass spectrometry, the peak used indicated in parentheses. Under these conditions[4] norbornene epoxide was produced preparatively in 98% yield, while benzil was recovered to the extent of 94%; thus the recovered diketone has been through the epoxidizing cycle an average of once per molecule. In view of this, comparison of the mechanistic requirements of Table I with the results of Table II shows that the mechanisms involving intermediates 3 and 5 in epoxidation must be ruled out. The species 4 remains eligible, provided that it is feasible for the coupling process shown in Scheme 3 to occur.[7] Every effort was made to insure anhydrous conditions; the 5-10% exchange in the sensitizer and 7% shortage of full exchange in the epoxide may well mean appreciable competition by a second mechanism.

Table II. Incorporation of ^{18}O During 15-Minute Photo-Epoxidation of Norbornene with $^{36}O_2$ Sensitized by Benzil and by Biacetyl

% Reaction (vpc)	% ^{18}O in Organic Products from Labeled O_2		
	Epoxide	Benzil	Biacetyl
(control)	----	5 ± 2 (m/e 105, 107)	
(control)	----		27 (m/e 86, 88, 90) 42 (m/e 43, 45)
70	93 (m/e 95, 97)	10 (m/e 105, 107)	
90	93 (m/e 95, 97)		8 (m/e 43, 45)

As previously observed, benzophenone is a very inefficient sensitizer for epoxidation compared to the α-diketones, but a mass spectrum on the very small amount of norbornene epoxide formed after 90 minutes of irradiation with benzophenone as sensitizer and conditions otherwise the same as in the experiments of Table II showed about 85% ^{18}O in the epoxide and about 18% in the benzophenone.

The control experiments of Table II, as well as the isotopic analyses on the recovered sensitizer, show that any photoequilibration leading to exchange of benzil or biacetyl with molecular oxygen is very slow compared to the sensitized epoxidation, for statistical equilibrium in these cases would lead to about 64% incorporation of ^{18}O in the diketone.

Possible nonradical mechanisms for photo-epoxidation include the initial formation of molecular complexes with various degrees of charge transfer between sensitizer and either oxygen or substrate.[8,9] Electron transfers are involved in an ingenious scheme proposed by Jefford and Boschung (Ref. 2, Scheme 7) for rose bengal-sensitized epoxidation, yet the epoxidation itself is attributed to a stepwise O-atom donation by hydroperoxy radical. Keay and Hamilton[10] have observed several epoxidizing species generated during the warm-up of 2-butyne ozonide, but despite the obvious relation of these species to α-diketone oxides, only low-yield (~5%) and stereo-specific epoxidation could be realized from diphenylacetylene ozonide[11] applied to β-methylstyrene. Since the highly efficient α-diketone sensitizers for epoxidation are strong electron-acceptors[12], it appears that the polarity of any complexation must be opposite to that attributed to rose bengal in the scheme for competitive epoxide and dioxetane formation.

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REFERENCES

1. P. D. Bartlett and M. S. Ho, J. Am. Chem. Soc., **96**, 627, (1974).
2. C. W. Jefford and A. F. Boschung, Helv. Chim. Acta, **60**, 2673, (1977).
3. P. D. Bartlett, Chem. Soc. Reviews, **5**, 154 (1976).
4. N. Shimizu and P. D. Bartlett, J. Am. Chem. Soc., **98**, 4193, (1976).
5. W. R. Wadt and W. A. Goddard II, J. Am. Chem. Soc., **97**, 3004, (1976).
6. P. D. Bartlett and M. E. Landis, J. Am. Chem. Soc., **99**, 3033 (1977).
7. The reaction of Scheme 3 is bimolecular, resembling the coupling of peroxy radicals that terminates the chains in autoxidation of cumene[13]. Such processes in monoradicals do not compete well with abstraction of tertiary benzylic hydrogen nor with addition to the unsubstituted end of a double bond; but in a case where neither of these propagating reactions was available[6] termination appeared to be a favorable path. It would seem that the formation of **4** itself must require the excited ketone to react with olefin initially in preference to reacting with oxygen, whose quenching constant toward triplet benzil or benzophenone has been measured as 1.4×10^9 (P. B. Merkel and D. R. Kearns, J. Chem. Physics, **58**, 398 (1973)). It is a fact, however, that saturation with oxygen does not impair the addition of excited benzophenone to tetramethylethylene to form an oxetane[4], which is generally regarded as proceeding through the same kind of biradical as **2**. It may be the concentration of the norbornene (which can be 50-100 times the solubility of oxygen in the solutions used) that enables it to compete for the triplet ketone.
8. J. Eriksen, C. S. Foote, and T. L. Parker, J. Am. Chem. Soc., **99**, 6455, (1977).
9. J. Eriksen, K. J. Lee, D. S. Steichen, and C. S. Foote, Abstracts of papers presented at 175th Natl. Meeting., Am. Chem. Soc., Anaheim, CA, 1978, No. ORGN 91.
10. R. E. Keay and G. A. Hamilton, J. Am. Chem. Soc., **98**, 6578, (1976).
11. N. Shimizu, unpublished work.
12. G. A. Russell in "Radical Ions," ed. by E. T. Kaiser and L. Kevan, Chap. 3, Interscience Publishers, New York, 1968.
13. J. A. Howard in Organic Free Radicals, W. A. Pryor, ed., ACS Symposium Series, No. 69, 1978, p. 413.

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