

incorrect.<sup>3e</sup> They have also inferred that substituents may alter the value of  $B_2^C$ . Thus, the results for 1-4 may be influenced adversely. However, the observed relationship can also be accommodated by the view that the geometry of the alkyl group alters during rotation through angle  $\theta$ . This suggestion is based on the fact that the values of  $\langle\theta\rangle$  derived from  $a_\beta^H$  for 1-4 do not, in general, correspond to conformations at potential energy minima. At the higher energy, steric interactions may increase the  $C_pC_\alpha C_\beta$  bond angle, lengthen the  $C_p-C_\alpha$  or  $C_\alpha-C_\beta$  bond, or more likely result in some combination of these deformations to decrease  $a_\beta^C$ .<sup>12</sup> With these ideas in mind we re-examined the results shown in Figures 1 and 2. Structural constraints in 5-8 restrict  $C_\beta$  to conformations which minimize steric repulsions. The  $a_\beta^C$  values for 5-8 very nearly conform to linear relationships. The data for 1-4 deviate from these relationships. However, these deviations may be related to structural deformations which are more significant for the cyclopropyl, isopropyl, and *tert*-butyl groups in 2-4 than for the ethyl group in 1. Further study will be necessary to verify these suggestions.

(12) The  $C_pC_\alpha C_\beta$  angle may decrease when  $\theta$  is small. This decrease may be attributed to steric factors or to electron transfer mechanisms; see, e.g., P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

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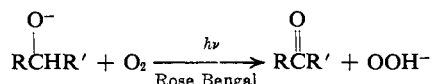
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## Oxidation of Alkoxides to Carbonyl Compounds by Singlet Oxygen<sup>1</sup>

Sir:

Singlet oxygen has been shown to react with nucleophilic substrates such as olefins,<sup>2</sup> amines,<sup>3</sup> sulfides,<sup>4</sup> and carbanions,<sup>5</sup> to produce products which vary with the nature of the substrate. We have now found that primary and secondary alkoxide ions are readily converted to aldehydes and ketones by dye-sensitized photooxidation.<sup>6,7</sup> The results are summarized in Table I.



(1) Work done on sabbatical leave at Yale University, 1972.

(2) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Amer. Chem. Soc.*, **90**, 975 (1968).

(3) W. F. Smith, Jr., *J. Amer. Chem. Soc.*, **94**, 186 (1972); M. H. Fisch, J. Gramain, and J. A. Oleson, *Chem. Commun.*, 663 (1971); G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957).

(4) C. S. Foote and J. W. Peters, *J. Amer. Chem. Soc.*, **93**, 3795 (1971).

(5) R. H. Young and H. Hart, *Chem. Commun.*, 827 (1967); R. H. Young, *ibid.*, 704 (1970); D. Bethell and R. G. Wilkinson, *ibid.*, 1178 (1970).

(6) The oxidations are generally accompanied by the formation of a white precipitate of alkali metal hydroperoxide except in methanol in which the alkali metal hydroperoxides are soluble.

(7) Earlier related work (e.g., G. O. Schenck and H. D. Becker, *Angew. Chem.*, **70**, 504 (1958); G. O. Schenck, H. D. Becker, K. H. Schulte-Elte, and C. H. Krauch, *Ber.*, 509 (1963)) was concerned with photooxidation of alcohols using benzophenone as sensitizer. These studies were carried out in the absence of base and the products were  $\alpha$ -hydroxy hydroperoxides. The mechanism, which seems to be well accepted, appears to involve reaction of oxygen with radicals produced by abstraction of hydrogen by triplet sensitizer.

Table I. Photooxidation of Alkoxide Ions<sup>a</sup>

Product	Base	Temp, °C	Yield, %
Acetone	Na	6-8	100 <sup>b</sup>
2-Butanone	<i>t</i> -BuOK	10	100 <sup>b</sup>
Cyclohexanone	<i>t</i> -BuOK	25-27	97 <sup>c</sup>
Benzophenone	KOH <sup>d</sup>	25-26	91 <sup>e</sup>
Formaldehyde	NaOH	2-5	61 <sup>c</sup>
Acetaldehyde	NaH	2-5	84 <sup>c</sup>
Butyraldehyde	NaH	2-5	61 <sup>c</sup>
Benzaldehyde	NaH	2-4	99 <sup>c</sup>

<sup>a</sup> Except where noted, excess of corresponding alcohol used as a solvent, and moles O<sub>2</sub> used = moles base. <sup>b</sup> Nmr analysis. <sup>c</sup> Isolation as 2,4-dinitrophenylhydrazone; some loss of yield owing to solubility in aqueous methanol medium used. <sup>d</sup> Mole ratio, 2.0 KOH:1.0 benzhydrol:0.50 O<sub>2</sub>, *t*-BuOH solvent. <sup>e</sup> Direct isolation.

In a typical reaction, a solution of 15.0 mmol of sodium isopropoxide in 115 ml of isopropyl alcohol containing 6 mg of Rose Bengal was irradiated internally by a 650-W DWY lamp operated at 100 V; 15.40 mmol of oxygen was absorbed within 55 min at 6-8°. Nmr analysis, using toluene as an internal standard, showed the presence of 15.0 mmol of acetone (2,4-DNP, mp 127-128°). The mixture was filtered under dry nitrogen, and the unstable, hygroscopic white residue was washed with isopropyl alcohol and dried *in vacuo* for 1 hr: Calcd for NaOOH: oxidation equivalent, 28.0; neutralization equivalent, 56.0. Found: oxidation equivalent, 31.9; neutralization equivalent, 59.4.

First-order dependence of the oxidation rate on isopropoxide ion was shown by a linear plot of log [(initial moles of RO<sup>-</sup>) - (moles of O<sub>2</sub> consumed)] vs. time for a constant temperature run at 9°. The intermediacy of singlet oxygen was indicated by the fact that the initial rate of oxygen uptake by a 1.5 × 10<sup>-2</sup> M isopropoxide solution containing either of the specific singlet oxygen quenchers  $\beta$ -carotene<sup>8</sup> (3 × 10<sup>-4</sup> M) or 1,4-diazabicyclo-[2.2.2]octane<sup>8,9</sup> (5 × 10<sup>-2</sup> M) was 30-40% of the rate observed in the absence of added quenchers. Under our conditions, oxidations of alcohols were never observed in the absence of either base, light, or sensitizer.

While secondary alcohol solutions became neutral after absorption of 1 equiv of oxygen and uptake of oxygen diminished to a negligible rate, primary alcohol solutions remained basic and continued to be oxidized at a moderate rate. This behavior may be related to a higher solubility of the basic sodium hydroperoxide in the more acidic<sup>10</sup> primary alcohols.

Photooxidation of primary alkoxides was complicated by the second-stage chemical oxidation of the initially formed aldehydes in the peroxidic reaction mixture. High conversion to carboxylate salts was observed after reaction mixtures from methoxide and ethoxide were allowed to stand for a few hours. The yields of aldehydes reported in Table I were achieved by photooxidation at low temperatures, followed by quenching with acidic dinitrophenylhydrazine solution.

Considering the electrophilic nature of singlet oxygen,

(8) C. S. Foote, R. W. Denny, L. Weaver, Y. C. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, **171**, 139 (1970).

(9) C. Ouannes and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968); R. H. Young and R. L. Martin, *ibid.*, **94**, 5183 (1972).

(10) J. Hine and M. Hine, *J. Amer. Chem. Soc.*, **74**, 5266 (1952).

