

THE PHOTSENSITIZED SINGLET OXYGEN ADDITION TO A SILYL ENOL ETHER

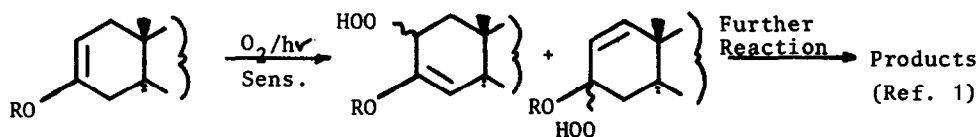
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The photosensitized oxygenation of enol esters has recently been shown<sup>1</sup> to afford products typical of the well documented<sup>2</sup> "ene" reaction of olefinic systems containing allylic hydrogens (Scheme I). We have prepared the

Scheme I



trimethylsilyl enol ether of isopropyl phenyl ketone 1 by standard procedures<sup>3,4</sup>, and subsequently studied the reaction of 1 with singlet oxygen.

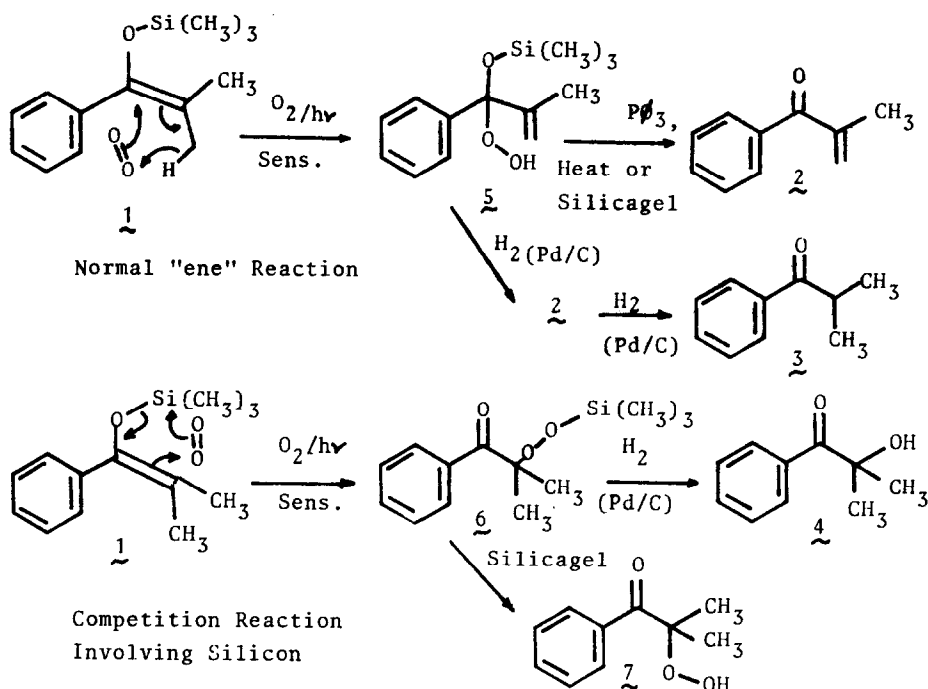
The irradiation in the presence of oxygen of 0.440 g (2mmol) of 1 in 5 ml of carbontetrachloride containing ca 2 mg of tetraphenyl porphyrin (TTP) as sensitizer<sup>5</sup> was complete in less than 0.5 hr as evidenced by nmr monitoring for disappearance of 1. The two component reaction mixture (nmr), which gave a positive potassium iodide test for the peroxide linkage, had the following spectral characteristics: ir (CCl<sub>4</sub>, cm<sup>-1</sup>) 3540, 3420 (O-H), 1685 (carbonyl); nmr (60 MHz) Hz (CCl<sub>4</sub>, TMS) 6 (s,9,Si-CH<sub>3</sub>), 9 (s,9,Si-CH<sub>3</sub>), 88-94 (broad,1,O-H), 88 (s,6,-CO-C(CH<sub>3</sub>)<sub>2</sub>), 94 (m,3,vinyl CH<sub>3</sub>), 296 (m,1, vinyl H), 320 (m,1,vinyl H), 426-492 (m,10,aromatic H). Gas chromatographic analysis<sup>6</sup> of the mixture gave irreproducible peaks, however, collection of the major peak showed it to be the  $\alpha,\beta$  - unsaturated ketone 2.<sup>7</sup>

Catalytic hydrogenation (Pd/C) in methanol of the oxidation mixture

obtained from 0.220 g (1mmol) of 1 afforded 0.291 g of a 62 : 35 : 3 mixture of 3, 4 and an unidentified compound. The structures of 3 and 4 were confirmed by comparison with authentic materials.<sup>8</sup> Further, treatment of the oxidation mixture with triphenyl phosphine in hexane at room temperature afforded 2<sup>9</sup>, while treatment with silica gel afforded a mixture of 2 and 7<sup>4</sup>, a derivative of 6. Control experiments show that 3 is inert to the oxygenation conditions and that 1 does not react in the absence of sensitizer.

We feel our results are compatible with Scheme II outlined below.

Scheme II



Oxygenation of 1 in the normal "ene" sense<sup>1,2</sup> affords the hydroperoxide 5 which is subsequently converted to 2 by thermolysis, triphenyl phosphine, silica gel or hydrogen. The reaction of 1 involving silicon migration affords 6 via a novel "ene" reaction<sup>10,11</sup> in direct competition with the normal "ene" reaction. We believe this to be the first example of such a successful competition, and in contrast to the reaction shown by enol

esters<sup>1</sup>. The scope of this novel silicon rearrangement is being explored with other silyl enol ethers.<sup>12,13</sup>

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References:

1. J. Pusset, D. Guenard, and R. Beugelmanns, Tetrahedron, 27, 2939 (1971).
2. C. S. Foote, Accs. Chem. Res., 1, 104 (1968).
3. H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, J.Org.Chem., 34, 2324 (1969).
4. The ir, nmr, and mass spectral characteristics are consistent with the proposed structure.
5. The irradiation source was a GE Quartzline (DVY-120v,650watt) light shining through an aqueous filter solution 0.2M in CuCl<sub>2</sub> and 0.5M in CaCl<sub>2</sub>. All irradiations were carried out at room temperature.
6. The analysis was carried out using an 8' 3%SE30 column at 130°C.
7. The compound was identical to 2 (nmr, glc retention time<sup>6</sup>) prepared by the method of J. H. Burckhalter and R. C. Fuson, J.Am.Chem.Soc., 70, 4184 (1948).
8. a.) Compound 3 was identical (ir, nmr, glc retention time<sup>6</sup>) to 3 prepared by the method of J. S. Swinehart, Organic Chemistry, an Experimental Approach, Appleton-Century-Crofts, New York, 1969, pp. 113-114.  
b.) Compound 4 was identical (ir, nmr, glc retention time<sup>6</sup>) to 4 prepared by the following sequence: Bromination of 1 by the method of J. Strating, S. Reiffers, and H. Wynberg, Syn., 1, 211 (1971); The  $\alpha$ -bromoketone<sup>4</sup> thus obtained was converted to 4 by the method of A. Favorski and A. Umnova, J.Russ.Phys.Chem., 44, 1380 (1912).
9. Nmr analysis.
10. For examples of silicon in a quasi-six member ring transition state see  
a.) A. G. Brook, D. M. MacRae, and W. W. Limburg, J.Am.Chem.Soc., 89, 5493 (1967).  
b.) L. H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill Book Company, New York, 1965, pp. 104-106.
11. The photosensitized oxygen addition of siloxy ketenals has been shown to involve a similar reaction pathway: W. Adam and J. C. Liu, J.Am.Chem.Soc., In Press.
12. Preliminary results indicate that the trimethylsilyl enol ether of pinacolone cleanly oxidizes to the corresponding  $\alpha$ -trimethylsilyl peroxy ketone analogous to compound 6.
13. Presented in part at the 11th Latin American Chemical Congress, Santiago de Chile, January 5-11, 1972.