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PHOTODESULFURIZATION OF O-ALKYL THIOESTERS

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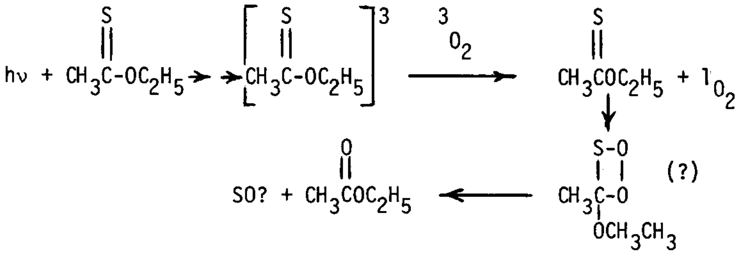
Abstract O-Ethyl thioacetate was shown to undergo exclusive conversion to ethyl acetate when photolyzed in the presence of oxygen in carbon tetrachloride solutions. The reaction parameters were explored.

A variety of unimolecular and bimolecular reactions have been observed upon the photolysis of O-alkyl thioesters under various conditions.[1,2] However, to our knowledge, nothing has appeared concerning the photochemical replacement of sulfur by oxygen even though various reports indicate this to be a facile process in thioketone photochemistry.[3] The recent interest in synthetic methodology for replacement of sulfur by oxygen in thioesters prompts our report of the photochemical replacement of sulfur by oxygen in O-ethyl thioacetate.[4]

Yellow O-ethyl thioacetate[5] was photolyzed with a medium pressure mercury lamp[6] in carbon tetrachloride solution (10%) through which oxygen was continually bubbled.[7] Ethyl acetate was the sole photoproduct (via nmr). To investigate the scope of this reaction, O-ethyl thiobenzoate[5] and O-ethyl thioformate[8] were irradiated under similar conditions. O-Ethyl thioformate gave a precipitate.[7] In our experience, this is typical of formate photochemistry and is probably due to free radical polymerization initiated by abstraction of the formyl hydrogen. The O-ethyl thiobenzoate gave no sign of reaction upon irradiation under the conditions which readily decomposed the O-ethyl thioacetate.[7]

Replacement of sulfur by oxygen in thioketones appears to proceed by formation of singlet oxygen.[3] An analogous mechanism for the ester reaction is shown below:[9]



$$h\nu + CH_3\overset{S}{\overset{\|}{C}}-OC_2H_5 \rightarrow \left[CH_3\overset{S}{\overset{\|}{C}}-OC_2H_5\right]^3 \xrightarrow{{}^3O_2} CH_3\overset{S}{\overset{\|}{C}}OC_2H_5 + {}^1O_2$$

$$SO? + CH_3\overset{O}{\overset{\|}{C}}OC_2H_5 \longleftarrow CH_3\underset{OCH_3CH_3}{\overset{S-O}{\overset{|\quad|}{C-O}}} \quad (?)$$

Carbon tetrachloride solutions of *O*-ethyl thioacetate (10%) were studied further in order to explore the reaction parameters. Photolysis for one hour gave 30% conversion of *O*-ethyl thioacetate to ethyl acetate. In recognition of the known chemiluminescent thermal oxygenation of thiocarbonyl compounds,[10] oxygen was added for one hour in the absence of light. A 10% conversion to ethyl acetate was observed. This thermal reaction was completely eliminated by the addition (10%) of known free radical trapping agents such as hydroquinone, 2,6-di-*tert*-butylphenol or n-dodecyl mercaptan. The one hour photochemical reaction in the presence of any of these materials gave $\sim$20% conversion to ethyl acetate. Adding either cyclohexa-1,3-diene (10%) or 1,4-diazabicyclo[2.2.2] octane (10%), to quench out a singlet oxygen reaction, along with n-dodecyl mercaptan reduced the photochemical yield to between 0 and 5%. Changing the solvent but otherwise maintaining similar conditions was particularly instructive. Results comparable to the carbon tetrachloride solution were obtained upon photolysis in nitrobenzene. Photolysis of neat ester showed an increased conversion to product at room temperature but no product formation at -60°. All other solvents (chloroform, methylene chloride, pyridine, acetone-d_6, benzene) gave no reaction during the one hour photolysis. These solvent effects are useful synthetically and also they are consistent with the singlet oxygen proposal (*vide supra*) since the lifetime of singlet oxygen is more than ten times greater in carbon tetrachloride (700 μsec) than in any of these latter solvents ($\leq$ 60 μsec).

References

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3. For example see J. J. Worman, M. Shen and P. C. Nichols, *Can. J. Chem.*, **50**, 3923 (1972).
4. D. H. R. Barton, J. J. Cussans and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 393 (1978).
5. A. Ohno, *Tetrahedron Lett.*, 2083 (1968).
6. Photolysis with a photoflood lamp gave comparable results.
7. Unless otherwise noted, control experiments were performed to rule out thermal reactions.
8. R. Mayer and H. Berthold, *Z. Chem.*, **3**, 310 (1963).
9. An explanation based on carbene formation via expulsion of atomic sulfur followed by oxygen capture by the carbene has precedent but is ruled out by the failure to trap atomic sulfur in related studies. See, for example, R. Jahn and U. Schmidt, *Chem. Ber.*, **108**, 630 (1975) and references cited therein.
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