Acknowledgment. We thank the National Science Foundation (CHE8009060; T.J.M.) for generous support of this research.

Registry No. 1, 82511-71-5; **2**, 82511-72-6; **3**, 82511-73-7; **4**, 82511-74-8.

Supplementary Material Available: Tables of fractional atomic coordinates and of anisotropic thermal parameters for nonhydrogen atoms of Th[η^5-$(CH_3)_5C_5$]$(CH_2C_6H_5)_3$ (**3**) (2 pages). Ordering information is given on any current masthead page.

Fluoride-Promoted, Dye-Sensitized Photooxidation of Enols

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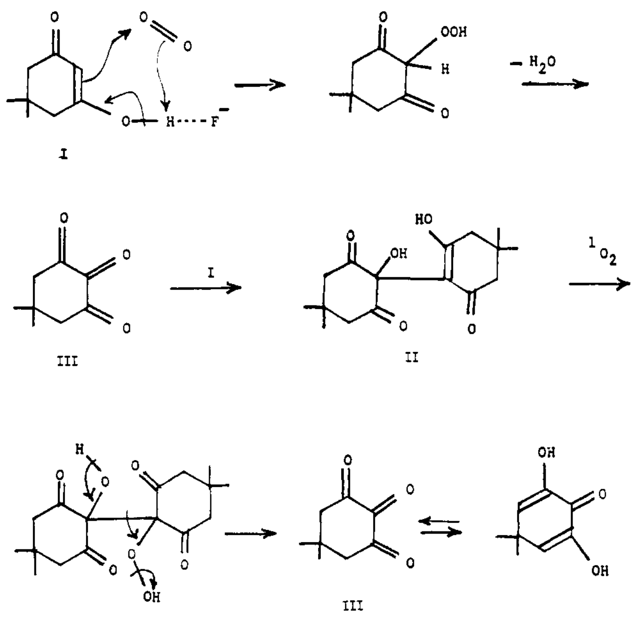
Among the reactions of singlet oxygen ($^1O_2$) with organic substrates, additions to carbon-carbon double bonds provide methods for the oxygenation of many types of compounds that have had numerous applications in synthesis.[1,2] The reactions of the electrophilic $^1O_2$ take place most readily with electron-rich systems such as enamines,[3,4] enol ethers,[5] and highly substituted olefins,[6] and the oxygenations of these substrates have been extensively investigated. By contrast, enolic tautomers of carbonyl compounds have received very little attention in singlet oxygen reactions beyond the observations that a few such compounds react slowly with $^1O_2$ to yield cleavage products.[7]

Recent findings showing that fluoride ion enhances the nucleophilicity of enols in alkylation and condensation reactions[8] prompted us to investigate the possibility of a related effect in enol-singlet oxygen reactions. It might be anticipated that hydrogen bonding or other electron-releasing phenomena associated with fluoride ion participation could operate to facilitate uptake of electrophilic $^1O_2$ by the donor enol component.

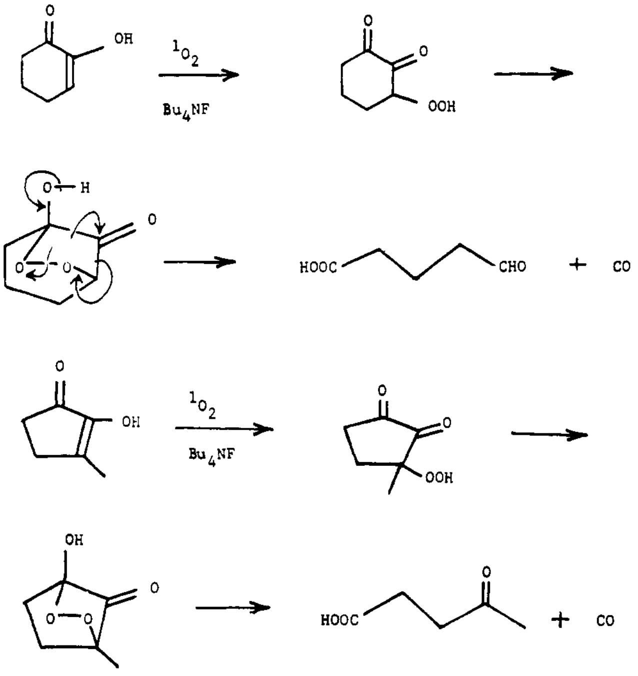
We now report a remarkable fluoride ion effect taking place in the reactions of a series of enolic compounds with $^1O_2$. Among the substrates are β-diketones, β-keto esters, and α-diketones. As is summarized in Table I, dye-sensitized photooxidations of all of these systems proceeded very sluggishly or failed completely in the absence of fluoride ion. In the presence of fluoride, however, the photooxidations were complete within a few hours, yielding ketonic products or other derivatives resulting from α-hydroperoxide formation.

In a typical procedure, the compound was dissolved in chloroform, tetrabutylammonium fluoride (1.1 equiv, as a 1 M solution in ethanol) was added, and the solvent was evaporated. The resulting oil was taken up in chloroform and injected into a dried, oxygen-purged well. Polymer-bound rose bengal[10] was added, and the solution was irradiated with visible light (650-W tungsten-halogen lamp, Pyrex-filtered) at 0 °C while O_2 was circulated. The course of the reaction was followed by O_2 uptake and by thin-layer chromatography. Workup consisted of filtration to remove the sensitizer and evaporation of solvent, followed by either partition between ether and water or chromatography on silica gel with chloroform.

Scheme I



Scheme II



Photooxidation of the β-dicarbonyl compounds shown in the table most probably takes place by an initial "ene"-type reaction followed by dehydration to a tricarbonyl compound which may then undergo hydration or enolization. With certain of the β-diketones studied, the triketone first formed appeared to take part in a second-stage reaction with unreacted starting material to yield an isolable intermediate. This product then underwent further oxygenation with $^1O_2$. This sequence is illustrated in the case of dimedone (I) (Scheme I) where oxidation with $^1O_2$ yielded the enolized triketone (III). Interruption of the reaction yielded II (the addition product of I and III), mp 133-134 °C,[12] which could

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(1) Wasserman, H. H., Murray, R. W., Eds. "Singlet Oxygen"; Academic Press: New York, 1979.

(2) Wasserman, H. H.; Ives, J. L. *Tetrahedron* **1981**, *37*, 1825.

(3) Foote, C. S.; Lin, J. W.-P. *Tetrahedron Lett.* **1968**, 3267.

(4) Wasserman, H. H.; Ives, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 7868.

(5) Bartlett, P. D.; Schaap, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 3223.

(6) Gollnick, K.; Kuhn, H. J. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 287-427.

(7) (a) Matsuura, T.; Matsushima, H.; Nakashima, R. *Tetrahedron* **1970**, *26*, 435. (b) Matsuura, T.; Matsushima, H.; Sakamoto, H. *J. Am. Chem. Soc.* **1967**, *89*, 6370. (c) Padwa, A.; Dehm, D.; Oine, T.; Lee, G. A. *Ibid.* **1975**, *97*, 1837.

(8) (a) Clark, J. H.; Miller, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 498. (b) Clark, J. H.; Holland, H. L.; Miller, J. M. *Tetrahedron Lett.* **1976**, 336. (c) Clark, J. H.; Miller, J. M. *Tetrahedron Lett.* **1977**, 599. (d) Clark, J. H.; Miller, J. M. *J. Chem. Soc., Trans. 1* **1977**, 1743, 2063.

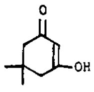
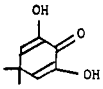
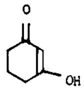
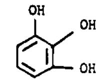
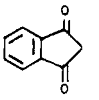
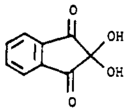
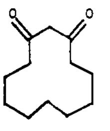
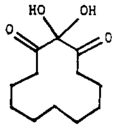
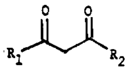
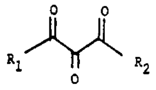
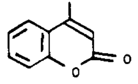
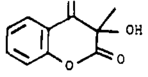
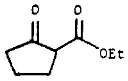
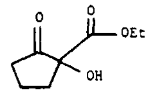
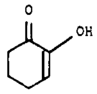
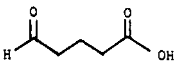
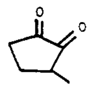
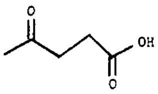
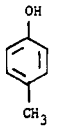
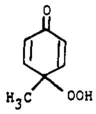
(9) Pless, J. *J. Org. Chem.* **1974**, *39*, 2644.

(10) Schaap, A. P.; Thayer, A. L.; Blossey, E. C.; Neckers, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 3741. Available commercially as Sensitox from Hydron Laboratories, New Brunswick, NJ.

(11) Clark, J. H.; Emsley, J. *J. Chem. Soc., Dalton Trans.* **1973**, 2154; **1974**, 1125.

(12) Product II, fully characterized by NMR, IR, and elemental analysis, could be prepared by addition of dimedone I to the triketone III.

Table I

dicarbonyl substrate	product[b]	yield with F⁻	results, absence of F⁻
		72%, 1½ h	a
		70%, 2 h	a
		75%, 3 h	b
		60%, 1 h	b
			
R_1 = Ph, R_2 = Ph	R_1 = Ph, R_2 = Ph	97%, 2 h	b
R_1 = Ph, R_2 = CH_3	R_1 = Ph, R_2 = CH_3[e]	72%, 3 h	b
R_1 = CH_3, R_2 = CH_3	R_1 = CH_3, R_2 = CH_3[e]	66%, 2½ h	b
		70%, ½ h	b
		49%, 2 h (2 equiv. F⁻)	b
	 + CO	65%, 3 h	c
		72%, 5 h	c
		87%, 3 h	a

[a] The reaction was very slow and yielded an intractable mixture of product. [b] There was no detectable oxygen uptake or change in TLC behavior after several hours of irradiation. [c] A very slow reaction, accompanied by severe dye bleaching. [d] Satisfactory NMR, IR, and elemental analyses were obtained for all new compounds. [e] Isolated as the addition product with *o*-phenylenediamine.

be further converted to 2 mol of III by reaction with $^1O_2$.

The α-diketone–singlet oxygen reaction also appears to take place by initial hydroperoxide formation. In the cases studied, these hydroperoxides undergo cyclization and cleavage as shown in Scheme II to yield aldehydo or keto acids along with carbon monoxide. Similar behavior has been observed in the photooxidation of flavones and coumaranones.[7a,b] In the absence of fluoride ion, the reaction was sluggish and severe dye bleaching occurred.

As noted in Table I, all of the compounds that were studied underwent photooxidation very slowly or not at all in the absence of fluoride ion. Tetraalkylammonium bromides and chlorides were not effective in accelerating the reaction. Potassium fluoride in the presence of 18-crown-6 does promote the photooxidations although a full equivalent of the crown ether is necessary for rapid reaction. When tetrabutylammonium hydroxide was used in place of the fluoride, uptake of oxygen took place at approximately the same rate, but complex mixtures of products were obtained as a result of base-catalyzed condensations and competing reactions of triplet oxygen in the alkaline medium.

We are giving further study to the role of fluoride ion in promoting these photooxidations and to the use of these tricarbonyl intermediates in synthesis. Clark and Miller[8,11] have proposed that the fluoride ion effect observed in the alkylation and condensation reactions of enols is associated with hydrogen-bonding phenomena leading to increased electron density on the enol oxygen. We believe that similar phenomena are responsible for the striking fluoride ion effect observed in the reactions of enols with singlet oxygen.

Acknowledgment. This work was supported by NIH Grant GM-13854. The support of the NSF/NMR Northeast Regional Facility at Yale University (Grant CHE-7916210) is acknowledged.

Registry No. I, 126-81-8; **II**, 81003-49-8; **III**, 32999-99-8; 2,6-dihydroxy-4,4-dimethyl-2,5-cyclohexadien-1-one, 78102-66-6; 3-hydroxy-2-cyclohexen-1-one, 30182-67-3; 1,2,3-benzenetriol, 87-66-1; 1*H*-indene-1,3(2*H*)-dione, 606-23-5; 2,2-dihydroxy-1*H*-indene-1,3(2*H*)-dione, 485-47-2; 1,3-cyclododecanedione, 6498-49-3; 2,2-dihydroxy-1,3-cyclododecanedione, 82415-36-9; 1,3-diphenyl-1,3-propanedione, 120-46-7; diphenylpropanetrione, 643-75-4; 1-phenyl-1,3-butanedione, 93-91-4; 1-phenyl-1,2,3-butanetrione, 4435-51-2; 2,4-pentanedione, 123-54-6; 2,3,4-pentanetrione, 921-11-9; 4-hydroxy-2*H*-1-benzopyran-2-one, 1076-38-6; 3-ethoxy-3-hydroxy-3,4-dihydro-2*H*-1-benzopyran-2,4-dione, 82415-37-0; ethyl 2-oxocyclopentanecarboxylate, 611-10-9; ethyl 1-hydroxy-2-oxocyclopentanecarboxylate, 82415-38-1; 2-hydroxy-2-cyclohexen-1-one, 10316-66-2; 5-oxopentanoic acid, 5746-02-1; 3-methyl-1,2-cyclopentanedione, 765-70-8; 4-oxopentanoic acid, 123-76-2; 4-methylphenol, 106-44-5; 4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one, 57749-82-3; tetrabutylammonium fluoride, 429-41-4.

Chemistry of Higher Order, Mixed Organocuprates. 4.[1] Stereochemical Outcome of Substitution Reactions at Unactivated Secondary Centers Using Organocopper Reagents

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Received May 19, 1982

Earlier reports[1,3] from these laboratories have demonstrated that the simple yet subtle shift from copper halide based organocuprates (i.e., R_2CuLi (**1**)) to copper cyanide derived species leads to a new class of highly reactive yet thermally stable[4] reagents of general formula $R_2Cu(CN)Li_2$ (**2**). These copper complexes react readily with α,β-unsaturated ketones in a Michael fashion[1]

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(1) Part 3. Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. *Tetrahedron Lett.*, in press.

(2) Recipient of an American Cancer Society Junior Faculty Research Award, 1981–1983.

(3) (a) Lipshutz, B. H.; Kozlowski, J.; Wilhelm, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 2305. (b) Lipshutz, B. H.; Wilhelm, R. S.; Floyd, D. M. *Ibid.* **1981**, *103*, 7672.

(4) Bertz, S. H., Bell Laboratories, private communication. "Abstracts of Papers", 183rd National Meeting, of the American Chemical Society, Las Vegas, NV, March, 1982; American Chemical Society: Washington, D.C., 1982; ORGN 110.

0002-7863/82/1504-4696$01.25/0