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**Supplementary Material Available:** Tables of fractional atomic coordinates and of anisotropic thermal parameters for nonhydrogen atoms of  $\text{Th}[\eta^5\text{-(CH}_3)_3\text{C}_5\text{]}(\text{CH}_2\text{C}_6\text{H}_5)_3$  (3) (2 pages). Ordering information is given on any current masthead page.

## Fluoride-Promoted, Dye-Sensitized Photooxidation of Enols

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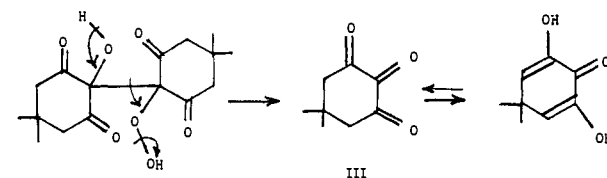
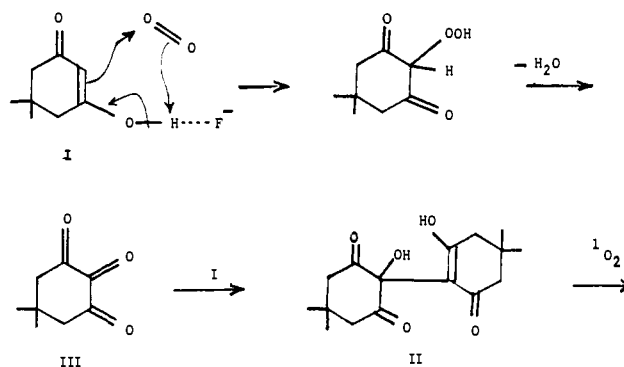
Among the reactions of singlet oxygen ( $^1\text{O}_2$ ) with organic substrates, additions to carbon-carbon double bonds provide methods for the oxygenation of many types of compounds that have had numerous applications in synthesis.<sup>1,2</sup> The reactions of the electrophilic  $^1\text{O}_2$  take place most readily with electron-rich systems such as enamines,<sup>3,4</sup> enol ethers,<sup>5</sup> and highly substituted olefins,<sup>6</sup> 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  $^1\text{O}_2$  to yield cleavage products.<sup>7</sup>

Recent findings showing that fluoride ion enhances the nucleophilicity of enols in alkylation and condensation reactions<sup>8</sup> 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  $^1\text{O}_2$  by the donor enol component.

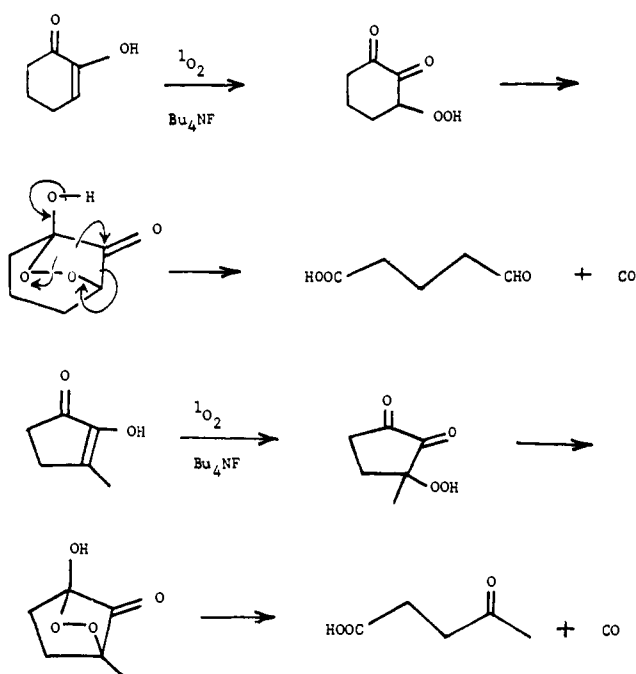
We now report a remarkable fluoride ion effect taking place in the reactions of a series of enolic compounds with  $^1\text{O}_2$ . Among the substrates are  $\beta$ -diketones,  $\beta$ -keto esters, and  $\alpha$ -diketones. As is summarized in Table I, dye-sensitized photooxidations of all of these 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  $\alpha$ -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<sup>10</sup> was added, and the solution was irradiated with visible light (650-W tungsten-halogen lamp, Pyrex-filtered) at 0 °C while  $\text{O}_2$  was circulated.

Scheme I



Scheme II



The course of the reaction was followed by  $\text{O}_2$  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.

Photooxidation of the  $\beta$ -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  $\beta$ -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  $^1\text{O}_2$ . This sequence is illustrated in the case of dimedone (I) (Scheme I) where oxidation with  $^1\text{O}_2$  yielded the enolized triketone (III). Interruption of the reaction yielded II (the addition product of I and III), mp 133-134 °C,<sup>12</sup> which could

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

