amide at \(-78^\circ\) 2 min after addition of ethyl acetate gives only 60\% recovery of ethyl acetate while quenching after 1 hr gives only 20\% recovery.

The synthetic potential of I is indicated by its reaction with cinnamaldehyde to produce a 94\% isolated yield of II (eq 3). The yields of \(\beta\)-hydroxy esters from other aldehydes and ketones are equally good as shown in Table I. This method for preparing \(\beta\)-hydroxy esters not only gives much higher yields than the usual Reformatsky procedure,\(^4,5\) but is much less time consuming as indicated by the following procedure for the conversion of cinnamaldehyde into I. A dry 100-ml flask equipped with septum inlet and magnetic stirrer was flushed with nitrogen. A solution of lithium bis(trimethylsilyl)amide in hexane was prepared by adding 2.95 mmol of cinnamaldehyde to a solution of lithium bis(trimethylsilyl)amide in hexane. The solution was then evaporated and replaced by tetrahydrofuran. The solution was allowed to reach room temperature, melted and exploded.

Figure 1. The position of the methyl triplet was studied by the conversion of other esters to the corresponding lithium derivatives.

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**Stereospecific Formation of 1,2-Dioxetanes from cis- and trans-Diethoxyethylenes by Singlet Oxygen**

SIR:

To the two modes of reaction of singlet oxygen, conjugate addition to dienes and allylic hydroperoxide formation,\(^1\) a third mode, formation of 1,2-dioxetanes, has recently been added.\(^2\) This reaction requires alkenes specially activated, as by amino\(^5\) or alkoxy\(^6\) groups, and the absence of very active allylic hydrogen in the molecule. Dioxetanes, whether prepared from singlet oxygen\(^7\) or by cyclization of halohydroperoxides,\(^8\) have been observed to decompose cleanly to carbonyl compounds with chemiluminescence.\(^4\) We report here evidence supporting stereospecific cis addition of singlet oxygen to vinylene diethers to give isolable dioxetanes as products.

\(\text{cis}\)-Diethoxyethylene (I), freed from its \(\text{trans}\) isomer by preparative vapor phase chromatography, 0.211 g, was dissolved in 7 ml of fluorotrichloromethane (Freon 11) which had been dried over molecular sieves. The solution, containing 10\(^{-4}\) \(M\) tetrphenyloporphin, was held in an acetone–Dry Ice bath at \(-78^\circ\) in a dewar with Pyrex windows and irradiated through a Corning uv filter with a 500-W lamp for 25 min in a stream of oxygen. Under these conditions white crystals began to form in 15–20 min, and soon filled the vessel. The crystalline dioxetane 2 was isolated by removing the Freon under vacuum through a sintered glass disk. A small sample of the product, on warming to room temperature, melted and exploded.

When the photooxidation of 1 was monitored by nmr, the ethylenic singlet of 1 at \(\delta 5.12\) gave way to a new singlet at \(\delta 5.91\). At the same time the methylene quartet of the ethyl group initially at \(\delta 3.73\) in 1 was further split because of the proximity of the new asymmetric carbon atom in 2, the signal in 2 being centered at \(\delta 3.88\). The 100-MHz nmr spectrum of 2 is shown in Figure 1. The position of the methyl triplet was

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**Communications to the Editor**
shifted only from δ 1.25 to 1.29. Under the conditions described the ethyl formate previously reported to accompany the dioxetane is not produced. Ethyl formate (5) appears either on prolonged irradiation in the presence of sensitizer or on warming to temperatures above 50° (k_i = 3.17 × 10^{-3} sec^{-1} at 54°) which converts the nmr spectrum of the solution completely to

\[
\begin{align*}
\text{H}_2\text{C} = \text{O} & \text{CH}_3
\end{align*}
\]

(1) h_r, O, CFC_3-TPP or CD_3CD_2-Rose Bengal

\[
\begin{align*}
\text{H} & \text{CH}_3
\end{align*}
\]

(3) h_r, O_2, CD_3CD_2-Rose Bengal

\[
\begin{align*}
\text{H} & \text{CH}_3
\end{align*}
\]

(5) HOCCH_3

\[
\begin{align*}
\text{H} & \text{CH}_3
\end{align*}
\]

(2)

that of 5 (singlet at 7.92, quartet at 4.18, triplet at δ 1.29). During the decomposition in benzene the broad ir absorption at 847 cm^{-1} decreased as the typical carbonyl stretch of ethyl formate appeared.\(^6\)

A molecular weight determination by isothermal distillation in Freon 11 at 2.6° against a dimethyl phthalate standard showed the dioxetane 2 to be monomeric (calcd volume of solution for monomer, 10.7 ml; for dimer, 7.3 ml; initial volume, 8.1 ml; volume after 30 min, 9.3 ml). The nmr spectrum showed no decomposition immediately after the molecular weight determination, but quantitative conversion to 5 after 30 min at 60°. A quantitative study of the luminescence quantum yield of the thermal decomposition of cis-dioxydioxetane 2 has been carried out and will be reported shortly.\(^6\)

Identical products resulted from photooxidation of 1 with tetraphenylporphin in Freon 11 and with Rose Bengal in deuterioacetone, as shown by the single nmr spectrum of a mixture of the two product solutions.

When trans-dioxyethylenyl (3) was photooxidized in deuterioacetone at -78°, a solution of 4 was obtained whose nmr spectrum had its singlet at 5.89 instead of the 6.15 observed for 2. Spectra of mixtures showed both peaks, but the photooxidation in deuterioacetone of each pure isomer yielded its own dioxetane unaccompanied, within the sensitivity of the nmr method, by the other.\(^7\) Each dioxetane decomposed quantitatively on warming to ethyl formate, \(k_{3 \rightarrow 5} = 1.40\).

First-order orbital symmetry theory leads to the prediction that singlet oxygen should not add suprafacially 1,2 to an alkene in a concerted manner.\(^8\) One anticipates therefore that dioxetane formation will be either stepwise or antarafacial (S_a + S_a).\(^9\) A stepwise biradical addition of singlet oxygen would be expected to lead to loss of configuration, but stepwise cycloadditions by way of dipolar ions show much more retention of configuration.\(^10,12\) The solvent susceptibility which we have reported\(^13,14\) for dioxetane formation \(k_{3 \rightarrow 5} / k_{3 \rightarrow 4}\) greater by a factor of 59 for acetonitrile than for benzene is inconclusive, being of a magnitude possible for a radical reaction with substantial polar character,\(^15\) or a concerted reaction with some charge transfer at the transition state.\(^13,14,15\)

A well-studied case of stereospecific 2 + 2 cycloaddition is that of ketenes.\(^16-18\) Singlet oxygen shares with ketene its unhindered linearity, which allows it to undergo antarafacial addition to an alkene. Although

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Figure 1. (a) 100-MHz proton nmr spectrum of recrystallized cis-dioxydioxetane in CFC_3; (b) same, expanded scale.

\[
\begin{align*}
\text{H}_2\text{C} = \text{O} & \text{CH}_3
\end{align*}
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(1) h_r, O, CFC_3-TPP or CD_3CD_2-Rose Bengal

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(3) h_r, O_2, CD_3CD_2-Rose Bengal

\[
\begin{align*}
\text{H} & \text{CH}_3
\end{align*}
\]

(5) HOCCH_3

\[
\begin{align*}
\text{H} & \text{CH}_3
\end{align*}
\]

(2)

(15) The proposal (Kearns, ref 8, footnote 51) of a peroxirane as a common intermediate in the formation of dioxetanes and allylic hydroperoxides might also accommodate the polar solvent dependence of dioxetane formation, although it does not predict the manner in which partition between these two products responds to the medium.

(15a) \textit{Note added in proof.} The substantial solvent effect on \(k_{3 \rightarrow 5} / k_{3 \rightarrow 4}\) for dihydroxypropyl is not observed in the rate competition between two symmetrical molecules, tetramethylcyclohexane, which gives only one reaction, and cis-dioxydioxetane, which gives only dioxetane (competition ratio in benzene, 0.82; in acetonitrile, 1.10). The most significant difference between these cases may be the symmetry of the substrate double bond.

Chemistry of Singlet Oxygen. IX. A Stable Dioxetane from Photooxygengation of Tetramethoxyethylene

Sir:

There has been much recent interest in 1,2-dioxetanes as possible intermediates in chemiluminescent reactions and in olefin photooxygengations. Electron-rich olefins are well known to undergo 1,2 cycloadditions with dienophiles, and enamines were found to undergo photosensitized oxidation to produce unstable intermediates which decomposed cleanly to carbonyl fragments. However, these intermediates were shown to be not solely monomeric 1,2 cycloadducts. The report by Hoffman and Häuser that the reactive olefin 1,1,2,2-tetramethoxyethylene (1) undergoes 1,2 cycloaddition suggested that photooxygengation of this compound might produce the dioxetane 1,2-dioxo-3,3,4,4-tetramethoxybicyclobutane (2).

Photooxygengation of 1 in ether, at —70 °C, sensitized by either zinc tetraphenylporphine or dinaphthalene-sensitized oxygen, can be envisioned, they may be discounted on the following grounds. Structure 3 and 4 can be envisioned as possible intermediates in chemiluminescent reactions and in olefin photooxygengations. Electron-rich olefins are well known to undergo 1,2 cycloadditions with dienophiles, and enamines were found to undergo photosensitized oxidation to produce unstable intermediates which decomposed cleanly to carbonyl fragments. However, these intermediates were shown to be not solely monomeric 1,2 cycloadducts.

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The ir spectrum (neat) had principal bands at 2980 (m), 2920 (w), 1440 (m), 1345 (m), 1210 (s), 1130 (s), 1065 (s), 1020 (w), 975 (w), 910 (m), 875 (w), and 830 cm⁻¹. Elemental analysis was consistent with the formula C₇H₁₀O₃ (Anal. Caled: C, 40.01; H, 6.71. Found: C, 40.02; H, 6.74). The molecular weight was determined to be 185 ± 6 (cryoscopic, benzene) and 198 (vapor pressure osmetry); the calculated value is 180. Iodometric determination showed 87 % of one peroxidic oxygen. When the product was heated at 56 °C in benzene in an nmr tube, a smooth decomposition occurred, yielding dimethyl carbonate (identified by ir, nmr, and vpc comparison with authentic material) as the sole product in quantitative yield.

These data are entirely consistent with dioxetane structure 2. Although alternate structures 3 and 4 can be envisioned, they may be discounted on the following grounds. Structure 3 would be expected to show two nonequivalent methoxyl resonances in the nmr (assuming oxygen inversion would be slow on the nmr time scale at —118 °C, the lowest temperature so far investigated). The equilibrium 4a ⇌ 4b, even if it were rapid enough to result in a single methoxyl resonance, should produce an averaged chemical shift considerably downfield from the observed position.

One of the most intriguing aspects of structure 2 is its close relationship to the CO₂ dimer (5), which has been implicated as the key intermediate in the chemiluminescent reaction of oxalyl halides and esters with H₂O₂, and to the suggested dioxetane interme-

(7) The dioxetane reported by Kopecky appears to be comparably stable, but no evidence for its structure or molecular weight has so far been published.

(7a) NOTE ADDED IN PROOF. The dioxetane has been characterized (E. H. White, J. Wiecko, and C. C. Wei, J. Amer. Chem. Soc., 92, 2167 (1970)).

(8) An approximate analogy may be found in the inversion rate of O-isopropylenglyoxonium fluoroborate, for which the coalescence temperature is ~50 °C; J. B. Lambert, ibid., 90, 1349 (1968).

(9) The average of the methoxyl shifts of trimethyl orthoformate (3.23 ppm) and of the dimethoxycarbonium ion [HC(OCH₃)₂]⁺ (4.64 ppm: see R. I. Borch, ibid., 90, 3503 (1968)) would be 3.93 ppm whereas the observed value is 3.45 ppm.