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# 3,3,7,7-BIS-(10'-METHYL-9',9'-ACRIDANYL)-1,2,5,6-TETRAOXOCANE, A DIOXETANE DIMER, FROM THE REACTION OF 10-METHYL-9-METHYLENE-9,10-ACRIDANE WITH SINGLET OXYGEN

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The methylene blue sensitized oxygenation of 10-Methyl-9-methylene-9,10-acridane (MMA) at -78°C yields three chemiluminescent compounds. The most stable compound, with a half-life at 0° of 15 min, is 3,3,7,7-bis-(10'-methyl-9',9'-acridanyl)-1,2,5,6-tetraoxocane, a dioxetane dimer. The most unstable compound, with a half-life at -60°C of 2 min, is believed to be the dioxetane of MMA. The compound of intermediate stability, with a half-life at -20°C of 5 min, is believed to be the zwitterion form of the ring opened dioxetane stabilized by a hydrogen bond to water (or, by choice, to some other weak acid).

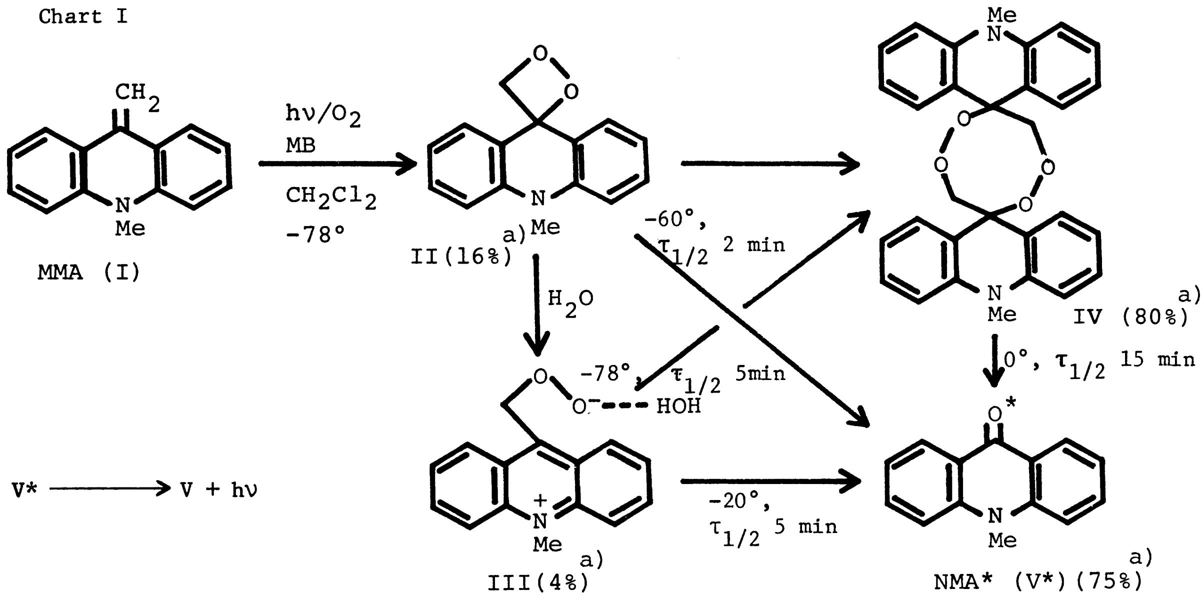
1,2-Dioxetanes and dioxetanones produce electronically excited states of carbonyl compounds on thermal decomposition.[1] The alkyl substituted dioxetanes and dioxetanones have been found to yield principally triplet excited states,[2] whereas the efficient chemi- and bioluminescent systems that appear to utilize dioxetanes and dioxetanones produce principally the singlet state.[3] To test whether the highly conjugated rings present in the latter systems might be responsible for the high singlet/tripelt ratio, we have examined the synthesis of dioxetanes that yield highly conjugated carbonyl compounds on decomposition. In this communication we report on the incorporation of the conjugated and fluorescent ketone, N-methylacridone (NMA, V)[4] into the dioxetane structure.

10-Methyl-9-methylene-9,10-acridane[5] (MMA, I, $10^{-3}$ -$10^{-6}$M) was irradiated at -78°C in dry, $O_2$-saturated $CH_2Cl_2$ containing methylene blue for 5 min to form the corresponding dioxetane, its open form, and the dimer. A plot of chemiluminescence intensity vs temperature upon warming up the mixture from -70° to +30°C with dry ice-ether bath revealed no less than three chemiluminescent species; maxima in intensity appeared at -60°C (II), -20°C (III), and 20°C (IV). Proposed structure for these compounds are given in Chart I.

Compounds III and IV yielded excited V on decomposition as shown by the UV absorption spectra of the reaction mixtures and by matching of the emission spectra ($\lambda_{max}$ ~430 nm in $CH_2Cl_2$) with the fluorescence spectrum of V. The color of chemiluminescence of the most unstable compound (II) was indistinguishable visually from the fluorescence color of V. The light emission is too short and weak to get spectrum.

Compound IV was isolated as a clolorless solid contaminated with 25-30% of V from a solution of the irradiation mixture passed over $CaCO_3$ to remove the methylene blue. Its structure as a dioxetane dimer (IV) rests on molecular weight and other physical measurements, elemental analysis,[6] and the reactions that it undergoes. Because of its lability, it was not obtained

Chart I



a) Yields from I.

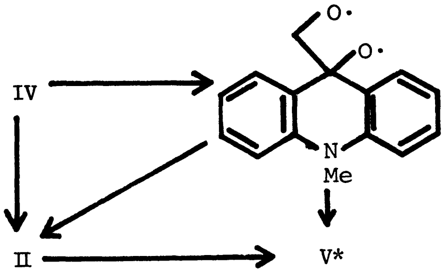
free of V; the amount of this contaminant was readily determined from the UV spectrum, however. The molecular weight of IV, measured by the freezing point depression of dry benzene solutions, and corrected for the presence of 30mole% of V, was 465 ± 40 (Theory for IV = 478.55). The freezing point of solutions that had been stored until decomposition of IV was complete, led to a mean molecular weight of 139 ± 10. A solution containing 2 molar equivalents of V, and formaldehyde would give an apparent molecular weight of 127, whereas if the formaldehyde were in the form of the trimer (trioxane) the mean molecular weight would be 183. The NMR spectrum, of IV in $CDCl_3$ at -10°C showed a broad singlet for the methylene group at 4.21 ppm from TMS and a singlet for the methyl group at 3.48 ppm; after decomposition, the methylene signal shifted to the value for formaldehyde trimer,[7] 5.18 ppm, and the methyl signal shifted to the value found for V, 3.99 ppm. The UV spectrum in $CH_2Cl_2$ shows a strong absorption at 278 nm ($\varepsilon$ 30,000); corresponding value for the model compound 9,9,10-trimethyl-9,10-acridane in EtOH are 278 nm (15,850).[8] The CIMS using isobutane and ammonia gave a peak at m/z 447 $(M-O_2 + H)^+$ which corresponds to $MH^+-O_2$; the intensities were 1.6 and 1.9%, respectively, of the base peak at m/z 210 $(NMA + H^+)$. FDMS gave similar peaks (m/z 446 (8.5%), 209 (100%)).

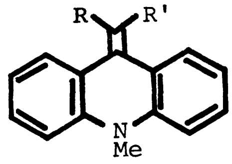
Decomposition at 20°C produced solely V (98.5% based on IV) and formaldehyde; the latter compound was detected as its dimedone derivative.[9]

Formation of III was accelerated by the action of water saturated $CH_2Cl_2$ on freshly prepared solutions of dioxetane II. Its UV spectrum ($\lambda_{max}$ 361 nm) was very similar to that of model acridinium salts.[10] Solutions of III upon warming (∿2°/min) led to a maximum in light emission at -20°C. When the solutions were stored at -78°C for 12 h, however, the ability to chemiluminesce at -20°C was lost —— with a commensurate increase in the light emission at 20°C (stemming from IV).

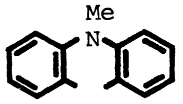
A dioxetane structure is proposed for compound II on the basis of its mode of synthesis, UV, and NMR at -95°C, conversion to III, formation of V* on decomposition, and its lability.

The quantum yield[11] of chemiluminescence from IV was found to be 0.015 einstein/mol. Since the fluorescence quantum yield of V in $CH_2Cl_2$ is 0.44,[4] the yield of singlet excited states has a minimum value of 0.034. Triplet counting led to a triplet quantum yield of 0.02.[4,12] These values are similar to those reported for an active species formed by the sensitized oxygenation of bisacridylidene (VIII) at -78° and proposed to be corresponding dioxetane.[4] The mode of formation of excited states from IV is of interest because of the *a priori* possibility that dioxetane II might not be an obligatory intermediate on the light path.





VIII: R + R' =



IXa: R=H, R'=$CH_2Ph$
b: R+R'=Adamantylidene
c: R+R'=4,4-Diphenyl-cyclohexadienylidene

Compound IV is apparently the first tetraoxocane to have been prepared and characterized. A tetraoxocane structure was listed as a possibility for the product of photooxygenation,[1a,13,14a] but the dioxetane structure was later proposed for the compound from dimethylisobutenylamine on the basis of molecular weight measurements.[14b] The capability of chemiluminescence of tetraoxocane systems was predicted by the EHMO calculation of the decomposition energy.[15] Recently, McCapra *et al*. reported that the reaction of several substituted olefins (IX) with singlet oxygen yielded chemiluminescent species which were proposed to be dioxetanes.[16] The stabilities of the oxygenated species from IXa and c were in the same range as that for IV; consequently, molecular weight measurements of these compounds would be of some interest.

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5) W. König, Chem. Ber., 56, 1543 (1923); $\nu_{max}$ (KBr) 1590, 1465 $cm^{-1}$; $\lambda_{max}$ ($CH_2Cl_2$) 383 ($\varepsilon$ 6900), 310 nm (8400); $\delta_{ppm}$ ($CDCl_3$) 3.45 (s, 2H), 5.28 (s, 2H), 7.00 (m, 4H), 7.28 (m, 2H), and 7.66 (m, 2H).

6) Found: C, 76.86%; H, 5.72%. Calcd. for 70% IV + 30% NMA ($C_{14}H_{11}NO$): C, 76.68%; H, 5.43%.

7) $\delta$ 5.1 ppm for s-trioxane in $CDCl_3$ (C. J. Pouchert and J. R. Campbell, "The Aldrich Library of NMR Spectra," Vol. 1, 156A, The Aldrich Chem. Co., Milwaukee, Wisc., 1974).

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9) mp 188.5-189.0° (lit. mp 189°; M. Frankel and S. Patai, "Tables for Identification of Org. Compds." 2nd ed., Chem. Rubber Co., Cleaveland, Ohio, 1964, p. 78; Rf ($CHCl_3$ elution) on silica gel = 0.87 and on alumina = 0.35.

10) 9,10-Dimethylacridinium methosulfate, $\lambda_{max}$ ($CH_2Cl_2$) 360 nm ($\varepsilon$ 7530); mp 232-233° (lit. mp 207°; S. Hünig and O. Rosenthal, Liebig's Ann., 592, 161 (1955)).

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