

Singlet oxygen oxygenation of enol ethers; the synthesis of optically active 1,2-dioxetanes. II

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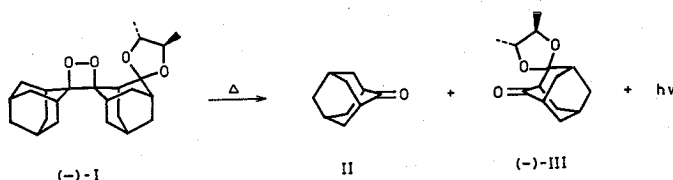
SINGLET OXYGEN OXIDATION OF ENOL ETHERS;
THE SYNTHESIS OF OPTICALLY ACTIVE 1,2-DIOXETANES-II

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Summary. Several chiral enol ethers, among which two derived from (+)-fenchone have been converted to (chiral) 1,2-dioxetanes by photosensitized oxygenation.

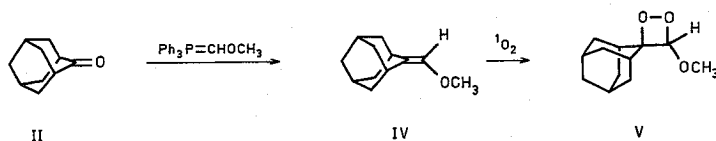
We have reported,^{1,2} the successful measurement of optical activity in chemiluminescence in the thermal decomposition of the optically active 1,2-dioxetane (-)-I as a result of the reaction shown:



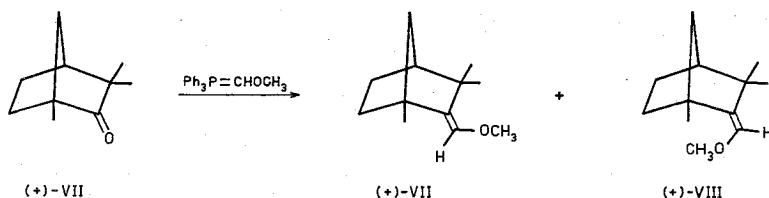
In this equation $h\nu$ represents emission from the first singlet state of the ketones II and (-)-III. Since one of the emitting species was chiral, we were able to measure the optical activity in chemiluminescence. In order to study this phenomenon in more detail it was essential that stable 1,2-dioxetanes could be constructed which would overcome one of the difficulties inherent in our first successful experiment, to wit: a second achiral ketone interfering with the polarized emission.^{2,3} One way to overcome this limitation is to prepare a 1,2-dioxetane, which decomposes either into one chiral ketone or into two fragments only one of which is ketonic. Several attempts have been made by us and by others to obtain stable 1,2-dioxetanes through the reaction of singlet oxygen with fenchylidene-fenchane³ and twistylidene-twistane.⁴

Both of these potential 1,2-dioxetanes would presumably decompose to yield one chiral ketone. However these attempts failed. In the present paper we describe the synthesis of 1,2-dioxetanes derived from enol ethers.^{5a,b,c} Decomposition of these 1,2-dioxetanes furnishes chemiluminescence emitted by one excited state ketone (a chiral molecule if desired).

The reaction sequence shown below for an achiral ketone, adamantanone, furnishes a reasonably stable 1,2-dioxetane and appears to be amenable to elaboration with chiral substrates.

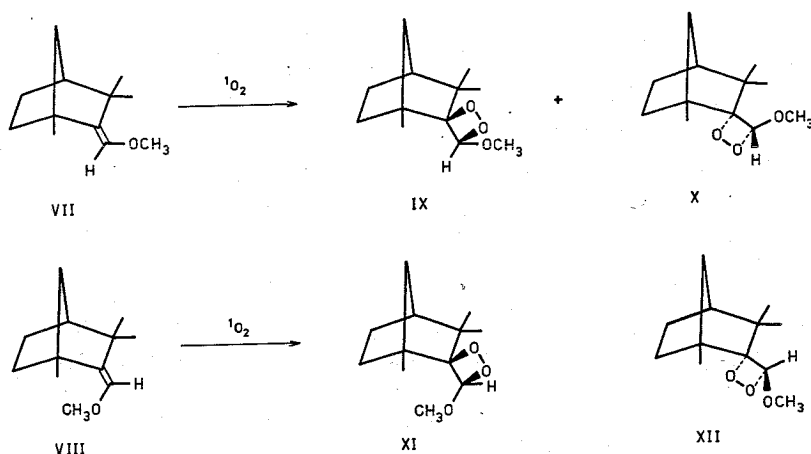


Methoxymethyleneadamantane IV was prepared in 75% yield as a colorless, odorless liquid (bp. 119°C/17 mm Hg; $n_D^{20} = 1.5148$) following the procedure described previously.⁶ Singlet oxygen oxidation (CH_2Cl_2 , methylene blue, 15°C) gave in almost quantitative yield the 1,2-dioxetane V. Further purification of V, for instance recrystallisation or chromatography over Al_2O_3 gave rapid decomposition.^{5a,7} The N.M.R. spectral data for V are: ^1H -N.M.R. (CDCl_3): δ 5.43 (1H,s), δ 3.43 (3H,s), δ 2.9-1.3 p.p.m. (14H,m); ^{13}C -N.M.R. (CDCl_3): δ 110.4(1C,s), δ 92.9(1C,s), δ 55.8(3C,q); δ 36 - δ 26 p.p.m. (9C,m). The thermal decomposition of V gave as only products adamantanone and methylformate and a bright blue chemiluminescence with $\lambda_{\text{max}} = 420$ nm and $k_1 = 2.96 \times 10^{-3} \text{ s}^{-1} (\pm 0.05)$ at 79.9°C in decane. The same reaction sequence can be followed for several chiral adamantanones⁸ and other ketones.⁹



For instance, the Wittig reaction on (+)-fenchone VI affords in 14% yield two isomeric enol ethers (+)-VII and (+)-VIII (2:1), which can be separated using H.P.L.C. (SiO_2 , hexane). The structures assigned are in accord with the spectral data.¹⁰ Singlet oxygen oxidation of VII gave in almost quantitative yield the two isomeric 1,2-dioxetanes IX and X. Similarly, oxidation of VIII affords the two isomeric 1,2-dioxetanes XI and XII. The ^1H -N.M.R. spectral data follows: The systematic shift of the proton at the 1,2-dioxetane ring to lower field [^1H -N.M.R. (CDCl_3):

isomer IX: δ 5.46; X: δ 5.55; IX: δ 5.86; XIII; δ 6.08 p.p.m.] is understandable in terms of an increase in the deshielding by the adjacent CH_3 group as the proton in question is forced into closer proximity to these alkyl groups. The ratios of IX and X (4:1) and of XI and XII (2.8:1), indicate a preference of singlet oxygen attack from the sterically least hindered site of the enol ether, in accordance with the results of Jefford.^{5a} The products of the thermal decomposition of IX and X are fenchone and methylformate and a bright blue chemiluminescence with $k_1 = 1.07 \times 10^{-3} \text{ s}^{-1}$ (± 0.05) at 79.9°C in decane.



The synthesis described above allows the preparation of 1,2-dioxetanes from a variety of ketones, in which a single ketone is the only chemiluminescent species at $\lambda_{\text{max}} = 420$ nm. This approach opens the possibility, that the light induced C.P.L. (circular polarization of luminescence) and the chemically induced C.P.L. can be compared. This comparison in turn allows an analysis of the conformation of a ketone in an excited state reached by different routes.^{11,12a,b}

References and notes.

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5. See for some 1,2-dioxetanes of enol ethers:
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9. The structure of the resulting enol ether must be such, that the ene reaction cannot take place.
10. Enol ether VII: $[\alpha]_{578}^{22} = +51^{\circ}$; IR: 1690 cm^{-1} ; $^1\text{H-N.M.R. (CDCl}_3)$: δ 5.56 (1H,s), δ 3.46 (3H,s), δ 1.19 (3H,s), δ 1.12 (6H,s), δ 1.8-1.1 p.p.m. (7H,m). Enol ether VIII: $[\alpha]_{578}^{22} = +117^{\circ}$; IR: 1690 cm^{-1} ; $^1\text{H-N.M.R. (CDCl}_3)$: δ 5.58 (1H,s), δ 3.44 (3H,s), δ 1.40 (3H,s), δ 1.04 (3H,s), δ 1.03 (3H,s), δ 1.8-1.1 p.p.m. (7H,m).
11. The light induced C.P.L. of fenchone has been measured, the chemically induced C.P.L. of the 1,2-dioxetanes IX, X, XI and XII is under investigation.
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