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8,9-DIOXA-6-METHYLBICYCLO(5.2.0)NONA-2,4-DIENE:
A 1,2-Dioxetane Formed by (2+2)-Cycloaddition of Singlet Oxygen to 7-Methyl-1,3,5-Cycloheptatriene.[1]

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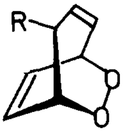
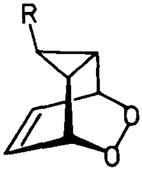
SUMMARY: Photosensitized oxygenation of 7-methyl-1,3,5-cycloheptatriene affords the title compound in ca. 15% yield, which represents the first 1,2-dioxetane derived from a cyclic conjugated polyene; its characterization, chemiluminescence, and mechanistic aspects are reported.

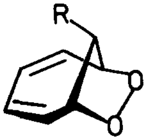
That cycloheptatriene is a versatile dienic substrate for singlet oxygen cycloaddition has been demonstrated, since the preparation of the tropilidene derived (2+4)-endoperoxide (1a),[3-5] norcaradiene derived (2+4)-endoperoxide (1b),[3,6] and the (2+6)-endoperoxide (1c)[3] have been recently reported. We have now succeeded in preparing, isolating and characterizing the 1,2-dioxetane (1d), formed by (2+2)-cycloaddition of singlet oxygen to 7-methyl-1,3,5-cycloheptatriene, thus completing the set of possible cycloadducts of 7-substituted-1,3,5-cycloheptatrienes. To the best of our knowledge, the unusual 1,2-dioxetane 1d represents the first example derived from a cyclic, conjugated polyene.



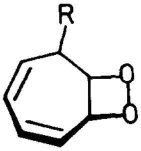
(1a)



(1b)



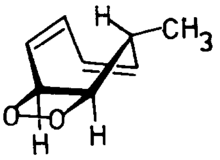
(1c)



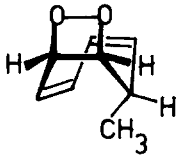
(1d)

On tetraphenylporphyrin (TPP)-sensitized photo-oxygenation of 7-methyl-1,3,5-cycloheptatriene in CCl_4 at 0°C as described previously,[3] after low temperature (ca. -40°C) chromatography, eluting with 1:1 CH_2Cl_2/n-pentane, the 1,2-dioxetane 1d ($R=CH_3$), i.e. 8,9-dioxa-6-methylbicyclo(2.2.1)nona-2,4-diene, was isolated in ca. 15% yield as thermally labile, colorless liquid, at least 95% pure by ^{1}H-NMR and iodometric titration.[7] The C^{13}-NMR ($CDCl_3$, -50°C)[8] reveals eight distinct resonances, the four sp^2 carbons at 133.81, 129.46, 128.13, 126.16 ppm, the dioxetane carbons[9] at 93.80 and 81.86 ppm, the ring-sp^3 carbon at 36.12 ppm, and the methyl carbon at 14.72 ppm.

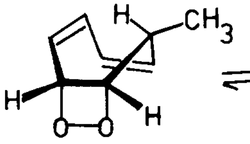
Although the C^{13}-NMR clearly establishes the claimed 1,2-dioxetane structure, the ^{1}H-NMR spectrum permitted the configurational and conformational assignment through double resonance experiments. Two configurations are possible, namely the anti- and the syn, which refer to the geometrical arrangement of the dioxetane ring with respect to the methyl group, and for each two conformations,



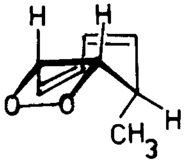
anti-e



anti-a



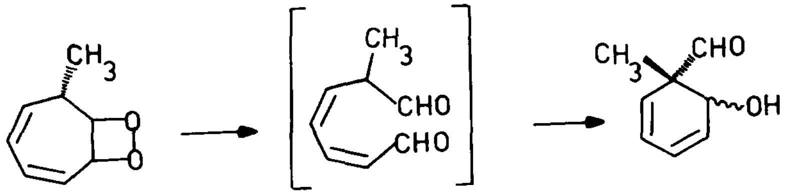
syn-a



syn-e

namely equatorial (e) and axial (a), which refer to the dioxetane arrangement with respect to the seven-membered ring, leading to a total of four structures that need to be scrutinized. The ^{1}H-NMR (CCl_4, TMS) exhibits proton resonances at δ(ppm) 1.05 (d, 3H, Me), 3.1-3.7 (m, 1H, H_6), 4.4-4.7 (dd, 1H, H_7), 5.2-5.7 (m, 4H, $H_{2,3,4,6}$) and 5.7-6.0 (br.d, 1H, H_1).[10] Irradiation of the Me at 1.05 ppm resolves the H_6 multiplet at 3.1-3.7 ppm into a double doublet with J_{67} = 10.33 and J_{65} = 3.99 Hz. Furthermore, irradiation of the H_6 multiplet at 3.4 ppm resolves the H_7 double doublet at 4.4-4.7 into a doublet with J_{76} = 10.33 and J_{17} = 6.99 Hz. Finally, irradiation of the H_7 proton at 4.4-4.7 ppm reduces the H_1 broad doublet at 5.7-6.0 ppm into a broad singlet. These ^{1}H-NMR data are most consistent with the anti (e)-conformer, especially on inspection of Dreiding models. For this conformer, the dihedral angle between H_6 and H_7 is ca. 180° which explains the large J_{67} value; however, the dihedral angle between H_1 and H_2 is ca. 90° and consequently the J_{12} value is small.

On warm-up to room temperature, the dioxetane 1d quickly decomposes with weak direct chemiluminescence.[11] The ^{1}H-NMR of the decomposition product is complex but consistent with structure 3, formed presumably via dialdehyde 2, the initial cleavage product of the dioxetane 1d, by intramolecular aldol condensation (eq. 1). Unfortunately, all efforts to isolate the exceedingly labile 3 even by low temperature (-50°C) silica gel chromatography failed.



1d 2 3 (eq1)

From the direct emission intensity we were able to determine the direct chemiluminescence yield[13] $\phi^{DC} = 1.13 \pm 0.02 \times 10^{-8}$ Einstein/mol. Unfortunately, no fluorescence data of the initial cleavage product 2 is available; besides, under the decomposition conditions 2 transforms into 3, so that no singlet excitation quantum yield ϕ^{S} can be calculated. However, from the low ϕ^{DC} value it should be evident that the singlet excitation yield is low.

To bypass this difficulty, we decided to evaluate the singlet excitation yield via enhanced chemiluminescence with 9,10-diphenylanthracene (DPA).[14] No light enhancement could be achieved with DPA. Similarly, neither DBA, used for the determination of the triplet excitation yield (ϕ^{T}), led to light amplification. Presumably the singlet excited states of DPA and DBA, respectively 72.9[15a] and 70.1[15b] kcal/mol, lie too high in energy to be effective for monitoring the singlet and triplet excited states of the intermediary 2. However, with rubrene enhanced chemiluminescence could be observed, but enhanced chemiluminescence did not operate via an electron exchange mechanism.[16] Quantitative measurements[14] of the chemienergized rubrene fluorescence afforded an enhanced chemiluminescence yield $\phi^{EC} = 9.0 \pm 0.8 \times 10^{-8}$ Einstein/mol at infinite rubrene concentration, extrapolated from a double reciprocal plot of the enhanced chemiluminescence intensity (I^{EC}) versus rubrene concentration. Since the rubrene fluorescence yield is unity under these conditions,[17] the singlet excitation yield (ϕ^{S}) is indeed very low for this dioxetane, i.e. ca. 10^{-5} %. Whether this very low singlet excitation yield relates to the fact that the lowest excited singlet of the dienic aldehyde chromophore in 2 may be of the π,π^* type[18] and that the dioxetane 1b avoids chemi-energizing such an excited state[19] is of course a relevant mechanistic question, which cannot be answered for the complex system under scrutiny here. Furthermore, we have so far not been able to evaluate the triplet excitation yield because no suitable low energy fluorescers are as yet available to us.

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7. The expected tropilidene and norcaradiene (2+4)-endoperoxides **1a** (R=CH$_3$) and **1b** (R=CH$_3$), respectively, were also obtained, but their characterization and transformations shall be reserved for a full paper on this subject. Furthermore, small yields of *ortho*- and *meta*-tolualdehydes were formed as well.
8. We are grateful to Prof. L.A. Paquette, Ohio State University and Prof. A. de Meijere, University of Hamburg, Germany for the low temperature ^{13}C-NMR spectra.
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