

# 1,2-Dioxetanes as chemiluminescent intermediates in the triplet oxygen oxygenation of olefins

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1,2-DIOXETANES AS CHEMILUMINESCENT INTERMEDIATES IN THE TRIPLET OXYGEN  
OXYGENATION OF OLEFINS.

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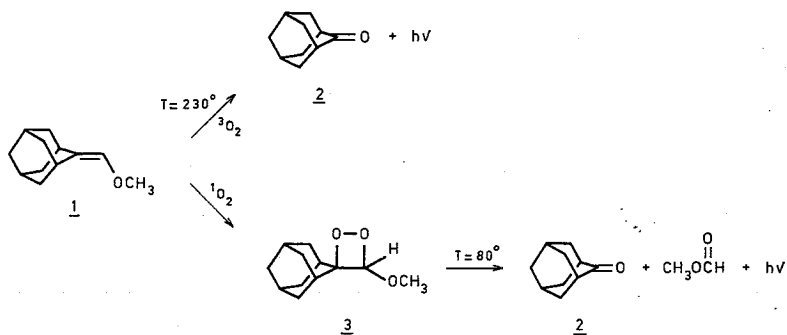
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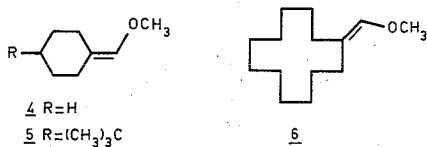
**Abstract:** *Several enol ethers react in the dark at elevated temperatures with triplet oxygen, producing ketones and chemiluminescence. Other electron-rich olefins were investigated.*

The current interest in the reaction of  $^1\text{O}_2$  (singlet oxygen) with olefins to produce 1,2-dioxetanes<sup>1</sup> prompts us to report our experience using  $^3\text{O}_2$  (triplet oxygen) at elevated temperatures.

Methoxymethyleneadamantane 1 reacts in the dark at a temperature of  $\sim 230^\circ\text{C}$  with atmospheric oxygen to produce adamantanone 2 in a good yield while a bright blue chemiluminescence (fluorescence of 2) is clearly visible. We have observed the same chemiluminescence ( $\lambda_{\text{max}} = 420 \text{ nm}$ ) in the thermal decomposition of the 1,2-dioxetane 3, synthesized by photooxygenation of 1.<sup>2</sup> Although the chemiluminescence produced by the reaction of 1 and  $^3\text{O}_2$  is (spectrally) identical with that produced by the thermal decomposition of 1,2-dioxetane 3, the latter occurs with a greater intensity. The resemblance of the two chemiluminescent reactions as well as the identity of the reaction product 2 makes it credible that the thermal oxygenation with triplet oxygen occurs via the 1,2-dioxetane 3. Attendant evidence for the similarity of the

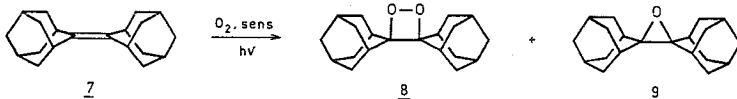


$^1\text{O}_2$  and  $^3\text{O}_2$  reaction is found in the oxidation of three other enol ethers. Recently Asveld and Kellogg have investigated the  $^1\text{O}_2$  oxidation of the enol ethers 4, 5 and 6 in several solvents.<sup>3</sup> Under all circumstances used, hydroperoxides (ene mode of reaction) as well as 1,2-dioxetanes were formed. When we heated the three enol ethers 4, 5 and 6 at  $230^\circ\text{C}$  in an oxygen atmosphere in the dark, the corresponding ketones could be isolated in two cases, while chemiluminescence was observed in all three cases.<sup>4</sup>



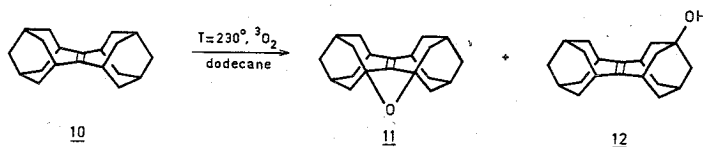
The experiments described above resemble the reaction of acetylenes and  $^3\text{O}_2$  reported by Turro.<sup>5</sup> A few examples of compounds, which give chemiluminescent reactions when brought in reaction solely with  $^3\text{O}_2$  have been reported.<sup>5-8</sup> In the reaction of  $^3\text{O}_2$  with strained acetylenes<sup>5</sup> and tetraaminoethylenes<sup>6</sup> respectively intermediate 1,2-dioxetene and 1,2-dioxetane formation has been proposed. In the autoxidation of cyclobutadienes<sup>7</sup> and ketenes<sup>8</sup> 1,2-dioxetanes have been detected.

Adamantylideneadamantane 7, when it reacts with singlet oxygen ( $\text{CH}_2\text{Cl}_2$ ; methylene blue as sensitizer) is converted quantitatively into adamantylideneadamantane-1,2-dioxetane 8.<sup>9</sup> However depending on the reaction conditions (solvent and sensitizer) the amount of the epoxide 9 varies.<sup>10</sup>

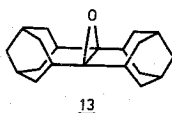


When a solution of 7 in dodecane is saturated with oxygen and heated in the dark at 230°C for two hours the products are adamantanone 2 (minor) and epoxide 9 (major). The yield of 9 can be raised to 60%.<sup>11</sup> Although in this reaction no chemiluminescence is observed, it is reasonable to suggest that 2 is formed from the intermediate 8. Remarkable is the phenomenon that samples of originally pure 7 contain small amounts of 8, after a normal storage for several months at room temperature.

A third olefin, which in principle can react with  $^1\text{O}_2$  without giving an ene mode of reaction is the eicosene 10.<sup>12</sup> Surprisingly 10 proved inert to  $^1\text{O}_2$ , generated chemically from triphenyl phosphite ozonide, and  $^1\text{O}_2$ , generated photochemically using methylene blue in  $\text{CH}_2\text{Cl}_2$ . The thermal oxidation of 10 in dodecane in the dark at 230°C affords as major products oxetane 11 (15%) and alcohol 12 (25%).<sup>13</sup>



No epoxide 13, which can be synthesized independently by *m*-chloroperbenzoic acid epoxidation, could be detected. It is plausible that the products 11 and 12 are formed via a radical mechanism.<sup>14</sup>



In summary, the oxidation of enol ethers 1, 4, 5 and 6 and adamantylideneadamantane 7 with  $^3\text{O}_2$  and  $^1\text{O}_2$  is remarkably similar. In the reaction with  $^1\text{O}_2$ , 1,2-dioxetanes are isolated. In the thermal reaction with  $^3\text{O}_2$ , 1,2-dioxetanes are proposed, as intermediates for this chemiluminescent reaction. Whether the reaction occurs via a  $^3\text{O}_2 \rightarrow ^1\text{O}_2$  conversion,<sup>5,8</sup> or via an electron transfer, following by a radical cage coupling and cyclization<sup>15</sup> is not clear.<sup>16</sup> Electron rich olefins, which proved to be inert to  $^1\text{O}_2$ , react in the known radical fashion with  $^3\text{O}_2$  at high temperature, as showed for eicosene 10.

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