

### 3,3-Dicyclopropyl-1,2-dioxetanes: Unusual Temperature Effect on the Singlet Oxygenation of 1,1-Dialkylethylenes

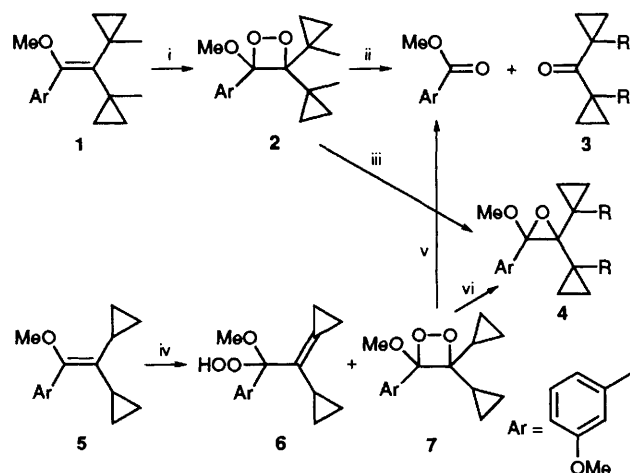
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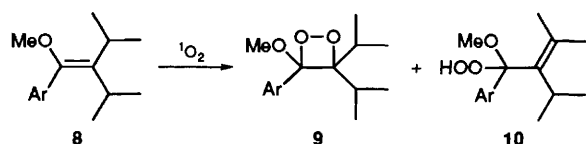
The reaction temperature has a significant effect on the singlet oxygenation of a vinylcyclopropane **5** to yield an allylic hydroperoxide **6** and a dioxetane **7**.

The reaction of vinylcyclopropanes with singlet oxygen has been intensively studied because of the interest in their electronic and steric characters. The main features of the oxygenation of vinylcyclopropanes have been reported as follows: the 'ene' reaction proceeds preferentially to give allylic hydroperoxides; and the 1,2-addition of singlet oxygen as the competitive mode occurs only rarely.<sup>1</sup> We now report that the reaction pathways of a vinylcyclopropane **5** with singlet oxygen are significantly affected by the reaction temperature; at low temperature, the preferential mode is the 1,2-addition to give a dioxetane **7**, whereas at high temperature, the 'ene' reaction occurs predominantly to afford an allylic hydroperoxide **6**. A similar temperature effect is observed in the oxygenation of an analogous 1,1-diisopropylethylene **8**.

We examined first the singlet oxygenation of a 1,1-bis-(1-methylcyclopropyl)ethylene **1** which should undergo only the 1,2-addition,<sup>†</sup> and tried to determine the stability of the dioxetane **2** formed. A solution of olefin **1** (100 mg) and tetraphenylporphine (5 mg) in dichloromethane (10 ml) was externally irradiated with a 940 W sodium vapour lamp under an oxygen atmosphere at 0 °C for 2 h. After the irradiation, the photolysate was concentrated *in vacuo* and the residue was chromatographed on silica gel. Elution with hexane-ethyl acetate (10:1) gave dioxetane **2** quantitatively, as a pale yellow oil. The reduction of the peroxide **2** with triphenylphosphine gave an epoxide **4** (R = Me) in 69% yield. The dioxetane **2** decomposed quantitatively into methyl *m*-methoxybenzoate and bis(1-methylcyclopropyl) ketone **3** (R = Me) in refluxing toluene, although it was fairly stable at lower temperatures ( $t_{1/2}$  = 105 h at 60 °C, 660 h at 45 °C).



**Scheme 1** Reagents and conditions: i,  $^1\text{O}_2$ ; ii, toluene, reflux; iii,  $\text{PPh}_3$ ; iv,  $^1\text{O}_2$ ; v, toluene, reflux; vi,  $\text{PPh}_3$



**Scheme 2**

Similar singlet oxygenation of dicyclopropylethylene **5** at 0 °C gave the hydroperoxide **6** as the main product, along with a dioxetane **7** ( $t_{1/2}$  = 2.1 h at 60 °C, 10.0 h at 45 °C) (**6**:**7** = 68:32). The structure of **7** was confirmed similarly to the case of **2** [reduction of **7** with  $\text{PPh}_3$  gave **4** (R = H); **7** decomposed in refluxing toluene to give **3** (R = H) and methyl *m*-methoxybenzoate (quantitative)]. At 25 °C, the oxygenation of **5** afforded a 78:22 mixture of **6** and **7**, while the dioxetane **7** was produced predominantly (**6**:**7** = 33:67) when the oxygenation was carried out at -78 °C. It is noteworthy that the reaction temperature has a significant effect on the mode of singlet oxygenation of the allylic olefins.

The following facts are well known for singlet oxygenation:<sup>3</sup> (i) the 'ene' reaction occurs preferentially for olefins possessing an allylic hydrogen which sometimes lies perpendicular to the plane of the double bond; and (ii) for most acyclic olefins possessing allylic hydrogens, the 'ene' reaction surpasses the 1,2-addition of singlet oxygen. These facts and the present results suggest that the cyclopropyl methine hydrogen(s) is far from being at a 90° dihedral angle with respect to plane of the double bond at low temperature (-78 °C).

A diisopropylethylene **8**, a structural analogue of **5**, was expected to be more affected than **5** by reaction temperature, because an isopropyl group is more sterically hindered than a cyclopropyl group. When the olefin **8** was similarly oxygenated at -78 °C, the corresponding dioxetane **9** ( $t_{1/2}$  = 99 h at 60 °C, 433 h at 45 °C) was produced in 95% yield, together with a hydroperoxide **10** in 5% yield. The oxygenation of **8** at 0 °C gave a 69:31 mixture of **9** and **10**, while at 25 °C a 29:71 mixture of **9** and **10** was produced.

It has been reported for molecules such as *N,N*-diisopropylamides and *N,N*-diisopropylthioamides that the interaction, the so-called 'gear effect', between two isopropyl groups at geminal positions makes some energy minima with respect to rotation of the isopropyl groups, and methine protons of isopropyls are far from being perpendicular to the trigonal plane at low temperature.<sup>4</sup> These facts can be equally applied to the present olefins,<sup>‡</sup> although the two isopropyls or cyclopropyls are attached to carbon instead of nitrogen.

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#### Footnotes

<sup>†</sup> It is also possible that, for olefin **1**, the 1,4-addition of singlet oxygen occurs to the conjugated system comprised of the ethylene and the aromatic ring.

<sup>‡</sup> In the NMR spectra of the olefins **1**, **5** and **8**, the temperature dependence (at 35 to -50 °C) was observed for the peaks due to methine protons of cyclopropyls in **5** and of isopropyls in **8**, and methyl protons of 1-methylcyclopropyls in **1**.

#### References

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