

presence of SOD. We also carried out the experiments in a well-dispersed heterogenous mixture of tetrahydrofuran and aqueous phosphate buffer (pH 7.8) containing rose bengal. Both the reactant and the product were monitored by gas chromatography. The solutions did not contain any free-radical inhibitor.¹³

The results are shown in Figure 2. The reaction was zero order with respect to **1** as expected,¹³ but was unaffected by the presence of the enzyme SOD within the limits of experimental detection. Even after the injection of the enzyme the rate of conversion of **1** to **2** remained the same. This indicates that there is a parallel mechanism for the generation of $^1\text{O}_2$ from rose bengal as compared to the production of O_2^- reported earlier.¹⁴

We performed similar experiments in the presence of SO_3^{2-} , to study the quenching effects of SO_3^{2-} on the $^1\text{O}_2$. The half-life of SO_3^{2-} in such solutions was quite short; yet for the first 10 min we were able to confirm that, indeed, $^1\text{O}_2$ is quenched by sulfite ions.

We conclude therefore that both the generation of O_2^- and of $^1\text{O}_2$ are possible from irradiated rose bengal in the presence of oxygen.

The quantum efficiency for the removal of oxygen by both the singlet oxygen path and the superoxide path can be calculated from the measured oxygen uptake in the presence and the absence of SOD, as well as with Dabco. If one writes the reactions, the relative efficiency of formation of singlet oxygen and superoxide can be calculated. Comparison of the slopes of 1B and 1D indicates that relative amounts are 77 to 23 in favor of $^1\text{O}_2$. This compares favorably with the values reported earlier by Schade and Gollnick.¹⁵ In accompanying studies, we have studied the photochemical reaction of $\text{Ru}(\text{bpy})_3^{2+}$ with SO_3^{2-} and oxygen.

We followed the oxygen uptake rate in $\text{Ru}(\text{bpy})_3^{2+}$, phosphate buffered sulfite solution both in the dark and with illumination (453 nm) as above. Similar studies with SOD and Dabco indicated the generation of O_2^- .

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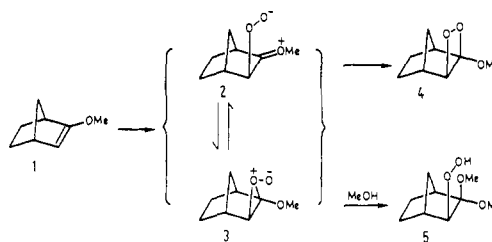
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Reaction of Singlet Oxygen with a Norbornadiene Ether. Intramolecular Interception of a Zwitterionic Peroxide

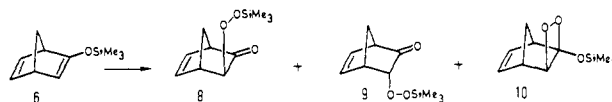
Sir:

Whether peroxides are intermediates in the reaction of singlet oxygen with monoolefins still remains problematic.¹ However, for electron-rich olefins, such as enamines² and enol ethers,³ evidence has been steadily accumulating that dioxetanes are formed in a two-step process.^{4,5} A pertinent example is provided by the photooxygenation of 2-methoxynorbornene (**1**) in the presence of methanol as an external nucleophile.⁶ The hydroperoxy ketal (**5**) is formed, whose origin is the short-lived zwitterionic peroxide **2** or its peroxide tautomer **3** which are intercepted by methanol before they collapse to the end product, the *exo*-dioxetane **4**. We now report that, by

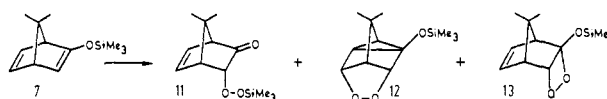


appropriately modifying the skeleton of **1**, the zwitterionic peroxide can be trapped intramolecularly. The molecules chosen are 2-trimethylsiloxy-2,5-norbornadiene (**6**) and its 7,7-dimethyl derivative (**7**).⁷ Their particular advantage is that a cationic center engendered by reaction with singlet oxygen should be captured by the norbornenyl double bond to produce nortricyclic products.⁹ Not only is this expectation realized, but all three possible modes of internal interception of the initially formed zwitterionic peroxide are exhibited.

Photooxygenation of the norbornadiene **6** in deuteriochloroform using *meso*-tetraphenylporphyrin as sensitizer at -20°C gave mostly the *exo*- α -silylperoxy ketone **8** (~80%), traces of its *endo* isomer **9** (<5%), and substantial amounts of the *exo*-dioxetane **10** (20%).¹⁰ The total yield was low (15–20%), as much polymeric material was formed. Reaction of the



7,7-dimethyl derivative **7**, under the same conditions, provided a dramatically different result. A clean, polymer-free, mixture of the expected *endo*- α -silylperoxy ketone **11** (64%) and a new tetracyclic peroxide **12** (36%) was formed. Careful scrutiny of the mixture by NMR spectroscopy at low temperature revealed traces of the *endo*-dioxetane **13** (<5%). Both **11** and



12 were isolated by column chromatography at low temperature and were readily identified by their NMR spectra.¹¹

These results are convincingly rationalized in terms of the formation of ionic intermediates as the primary event. Attack by singlet oxygen on the parent norbornadiene **6** takes place preferentially on the less hindered *exo* face of the molecule to give the zwitterionic peroxide **14** or its tautomer **15**. Subse-

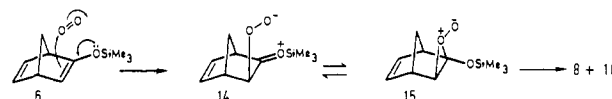


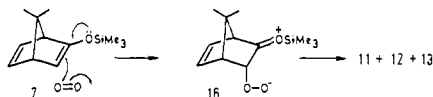
Table I. Relative Rates of Photooxygenation of 2-Siloxybornenes

acceptor ^a				
<i>K</i> _{rel}	17	8.4	4.2	1

^a R = SiMe₃.

quently, the peroxide ion has the choice of removing the easily detachable silyl group to give **8** or closing to the dioxetane **10**. The same process occurs to a lesser degree on the endo face of **6**. The endo zwitterionic peroxide gives mainly the product of silatropic rearrangement, **9**. The corresponding *endo*-dioxetane is simply not detected, presumably owing to its even lower concentration than that of **9**.

The action of the *gem*-dimethyl grouping at C-7 is to force singlet oxygen to approach the endo face of the norbornadiene skeleton. This time the resulting zwitterionic peroxide **16** has three avenues of reaction available. Silatropic shift, as before, is favored over dioxetane formation. However, an alternative



is provided, as charge is also conveniently annihilated by closure to the *endo*-peroxynorbornene derivative **12** which, incidentally, could be regarded as the consequence of a non-concerted homo-Diels-Alder addition. The isolation and stability of **11** and **12** at room temperature rule out concerted formation of **12** followed by equilibration to **11**.

One last, but important point, concerns reaction rates. Both **6** and **7** reacted rapidly with singlet oxygen; solutions (0.5 M) in deuteriochloroform containing *meso*-tetraphenylporphyrin (~10⁻³ M) were quantitatively oxidized in 5 min. Moreover, the usual tests confirmed the intermediacy of singlet oxygen as reagent.¹² Rates of **6** and **7** were also compared with their monoolefinic counterparts (Table I). It is significant that dienes react faster than monoenes and that the presence of methyl groups at C-7 is rate retarding.¹³ This behavior parallels exactly that of 2-methylnorbornadiene and its 7,7-dimethyl derivative, where singlet oxygen reacts to give the allylically rearranged hydroperoxide.¹⁴ Consequently, in the present case it can be similarly concluded that singlet oxygen is behaving as an electrophile and that the transition state is controlled essentially by the HOMO of the siloxy olefins, modified by a steric effect.

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- ¹H NMR analyses are fully consistent with those previously reported for *exo*- and *endo*-α-silylperoxynorbornanes (see ref 6). **11** (CDCl₃): δ 0.2 (9 H, s, Si(CH₃)₃), 1.10 (6 H, s, 2CH₃), 2.8 (1 H, m, H-C(1)), 2.9 (1 H, m, H-C(4)), 4.72 (1 H, d, J_{3,4} = 3 Hz, H-C(3-*exo*)), 5.96 (1 H, dm, H-C(6)), 6.50 (1 H, dd, J_{6,5} = 6 Hz, J_{6,1} = 3 Hz, H-C(5)). **8** (CDCl₃): δ 0.2 (9 H, s, Si(CH₃)₃), 2.22 (1 H, dm, J_{7,7} = 10 Hz) and 2.42 (1 H, dm, J_{7,7} = 10 Hz) (H-C(7a, 7s)), 2.98 (1 H, m, H-C(1)), 3.38 (1 H, m, H-C(4)), 4.08 (1 H, dd, J = 3, 1 Hz, H-C(3n)), 6.21 (1 H, ddt, J_{5,6} = 6 Hz, J = 3, 1 Hz, H-C(6)), 6.44 (1 H, dd, J_{5,6} = 6 Hz, J = 3 Hz, H-C(5)). **9** (CDCl₃): spectrum identical with that of **11** except d at 4.48 (1 H, J = 3 Hz, H-C(3x)) instead of dd at δ 4.08. **11** and **9** are readily reduced to the corresponding α-siloxybornenes by treatment with 1 equiv of triphenylphosphine. The decoupled ¹H NMR spectrum for peroxide **12** is unambiguous: δ 0.2 (9 H, s, Si(CH₃)₃), 0.96 (3 H, s, CH₃), 1.16 (3 H, s, CH₃), 1.6 (1 H, dd, J_{1,6} = 6 Hz, J_{1,4} = 2.5 Hz, H-C(1)), 1.72 (1 H, dm, J_{1,6} = 6 Hz, H-C(6)), 2.32 (1 H, m, H-C(4)), 4.78 (1 H, d, J_{3,4} = 3 Hz, H-C(3)), 4.84 (1 H, dd, J_{4,5} = 3 Hz, J_{5,6} = 2 Hz, H-C(5)).
- Proof for reagent singlet oxygen was obtained by testing oxygenation in the absence of light, sensitizer, oxygen, and by adding Dabco as well as noting the effect of deuterated solvent.
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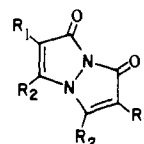
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1,5-Diazabicyclo[3.3.0]octadienediones (9,10-Dioxabimanes). Strongly Fluorescent Syn Isomers

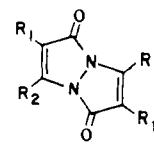
Sir:

We herewith report the existence of an essentially new class of stable heterocyclic molecules, of elegant and simple structures, derived by surprisingly straightforward means from commonly available compounds and marked, in one series of isomers, by a beautiful and striking fluorescence. We now describe the synthesis and some chemical reactions. The X-ray structural determinations¹ and the photophysical properties² will be reported later.

In attempts to prepare 2-octadecynoic acid via treatment of a dichloropyrazolone with strong base,^{3,4} we noted the formation of a strongly fluorescent compound in small yield. Spectroscopic and analytical data suggested an unusual structure, and we were able to develop a procedure (heterogeneous base treatment of a concentrated solution of halopyrazolone in a suitable organic solvent) which has given up to 67% yield of the fluorescent isomer along with up to 10% of the weakly fluorescent isomer. The isomeric compounds are 1,5-diazabicyclo[3.3.0]octadienediones, the *syn* isomer being strongly fluorescent (emission maxima 388-520 nm, depending upon substitution and solvent, quantum yields 0.7-0.9), and the *anti* isomer weakly fluorescent. The structures have been confirmed by X-ray crystallography. Since the compounds are usually quite symmetrical, we have adopted the brief name



syn-(R₂, R₁) B



anti-(R₂, R₁) B