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THE ADDITION OF SINGLET OXYGEN TO ALKOXY AND TRIMETHYSILOXYBUTADIENES. THE SYNTHESIS OF NOVEL NEW PEROXIDES.

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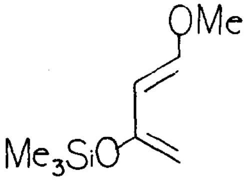
Summary: The additions of singlet oxygen to four 1,3-dienes are reported. Spectral studies of the reaction products corroborate their suggested structures. Hydrolysis of these products resulted in the formation of several novel new peroxides.

In the past five years the use of siloxybutadienes in 4+2 cycloadditions has attracted considerable attention.[1] The appeal of these diene substrates is in part due to the presence of the latent carbonyl functionalities in the cycloadducts which can be utilized for additional transformations. The Danishefsky group in particular have utilized these dienes in a number of elegant total syntheses.[2] In addition to the commonly utilized hydrocarbon dieneophiles, heterodieneophiles such as aldehydes,[3] ketones,[4] and imines[5] have also been shown to react smoothly with these substrates.

In conjunction with our program to synthesize and explore the properties of novel new peroxides we report the successful addition of singlet oxygen to dienes 1-4. The additions of singlet oxygen to dienes 1,[6] 2,[7] and 3[8] proceeds smoothly to give the 4+2 cycloadducts with only trace amounts of by-products. In contrast, the reaction of 4[9] produced a 25% yield of a non-peroxidic material in addition to the endoperoxide. This material was identified as phenoxytrimethylsilane 5 by comparison of its spectral properties to that of an authentic sample. We envisioned that formation of this product occurred by one of two ene reactions followed by elimination of hydrogen peroxide as shown in Scheme I. Monitoring the reaction progress at -76°C by low temperature ^{13}C NMR demonstrated that a symmetrical intermediate, (^{13}C NMR δ 130.81 (d, J =



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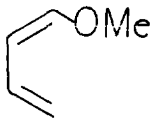

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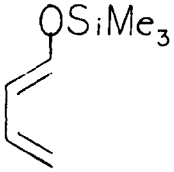

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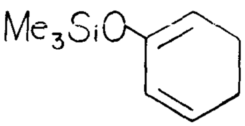

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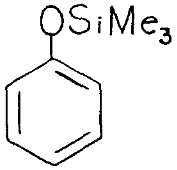

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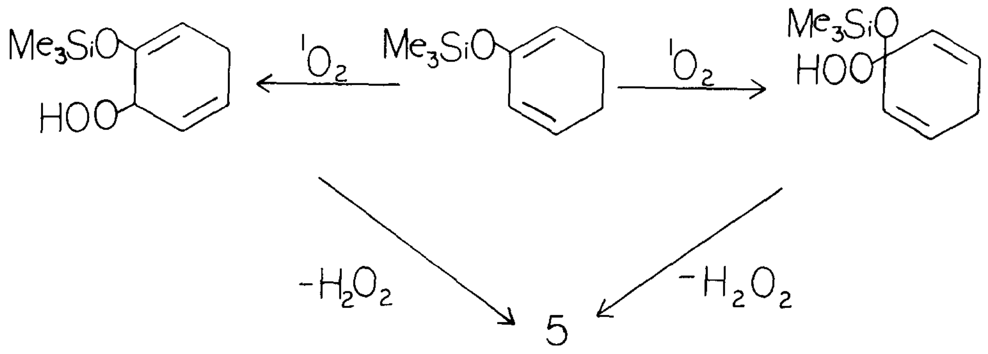
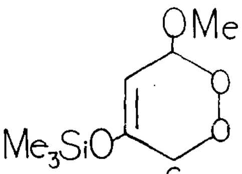
Scheme I.



164 Hz), 125.48 (d, J = 166 Hz), 96.72 (s), 27.84 (t, J = 125 Hz)) was formed which decomposed to 5 on warming to room temperature. This result demonstrates that the ene reaction occurs at the electron rich double bond.

In general the last step[10] in peroxide synthesis is the introduction of the peroxide linkage. The extreme ease in which peroxides undergo induced decomposition[11] precludes many subsequent synthetic manipulations. The mildness of the desilylation process, however, suggests tha endoperoxides 6-8 may be amenable to further functional group transformations. This speculatio proves to be correct. Hydrolysis of 6-8 by the procedure of Danishefsky (4:1 THF/0.005 M HCl)[12] produced the novel peroxides 10-12, respectively. All of our attempts to date to produce the vinyl peroxide 13 from 6 have failed. The properties and reactivity of these novel new peroxides are currently under investigation and the results of these studies will be reported in the near future.



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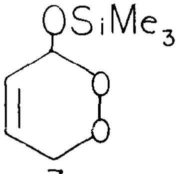

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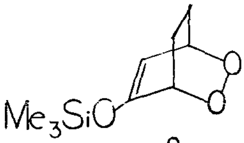

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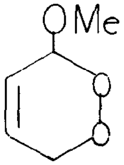

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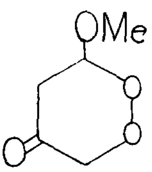

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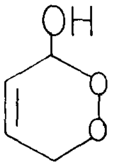

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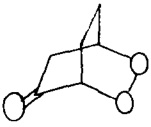

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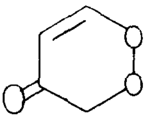

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A typical synthetic procedure for the addition of singlet oxygen is as follows: A solution of 2.46 g (14.3 mmole) of diene 1 and 10 mg of TPP in 60 ml of dry methylene chloride was saturated with oxygen. The mixture was cooled to -78°C using a dry ice acetone bath and photolyzed with a 750 W lamp through a sodium nitrite filter for 10 hrs. The progress of the reaction was monitored periodically by ^{1}H NMR. After disappearance of the starting material the crude reaction mixture was warmed to room temperature and the solvent removed at 0°C. The endoperoxide was obtained by flash chromatography[13] of the residue and vacuum distillation of the column eluent. The chemical and physical properties of the endoperoxides are:

6 ^{1}H NMR ($CDCl_3$) δ 5.12 (d, J = 3.7 Hz, 1 H), 5.00 (dd, J = 3.7, 1.5 Hz, 1 H), 4.3 (d, J = 16.1 Hz, 1 H), 4.06 (dd, J = 16.1, 1.5 Hz, 1 H) 3.50 (s, 3 H), 0.26 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 152.96 (s), 99.93 (d, J = 162 Hz), 98.02 (d, J = 162 Hz), 71.19 (t, J = 142 Hz), 55.83 (q, J = 142 Hz), 0.43 (q, J = 119 Hz) IR (neat) 2956 (m), 2893 (m), 2827 (m), 1675 (s), 891 (s), 844 (s). Mass spectrum: Found 204.08190 Calc. 204.08014 bp. 40-45°C (0.1 mm Hg) 28% isolated yield.

7 ^{1}H NMR ($CDCl_3$) δ 6.16 (dd, J = 10.3, 4.4 Hz, 1 H), 5.92 (bd, J = 10.2 Hz, 1 H), 5.42 (d, J = 2.9 Hz, 1 H), 4.75 (bd, J = 16.8 Hz, 1 H), 4.33 (dd, J = 16.8, 4.4 Hz, 1 H), 0.23 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 126.97 (d, J = 164 Hz), 125.02 (d, J = 166 Hz), 92.31 (d, J = 152 Hz), 68.94 (t, J = 144 Hz), 0.11 (q, J = 119 Hz). IR (neat) 3052 (w), 2955 (s), 2881 (s), 1654 (w), 1107 (s), 886 (s), 837 (s). Mass spectrum: Found 174.06750 Calc. 174.07052 bp. 48-50°C (2mm Hg) 34% isolated yield.

8 ^{1}H NMR ($CDCl_3$) δ 5.45 (dd, J = 7.0, 2.2 Hz, 1 H), 4.73 (m, 1 H), 4.41 (m, 1 H), 2.2 (m, 2 H), 1.56 (m, 2 H), 0.28 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 154.59 (s), 102.78 (d, J = 168 Hz), 75.79 (d, J = 153 Hz) 72.50 (d, J = 151 Hz), 23.89 (t, J = 135 Hz), 21.94 (t, J = 135 Hz), -0.025 (q, J = 120 Hz). IR (neat) 2957 (s), 1642 (s), 904 (s), 844 (s). Mass spectrum: Found 200.08750 Calc. 200.08688 29% isolated yield.

9 ^{1}H NMR ($CDCl_3$) δ 6.22 (ddd, J = 10.2, 4.4, 1.5 Hz, 1 H), 5.93 (ddd, J = 10.2, 2.9, 1.5 Hz, 1 H), 4.95 (d, J = 2.9 Hz, 1 H), 4.78 (ddd, J = 16.8, 1.5, .73 Hz, 1 H), 4.31 (dd, J = 16.8, 4.4 Hz, 1 H), 3.53 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ 128.44 (d, J = 160 Hz), 122.54 (d, J = 170 Hz), 98.37 (d, J = 162 Hz), 69.07 (t, J = 144 Hz), 55.75 (q, J = 142 Hz). IR (neat) 2953 (m), 2931 (m), 2883 (m), 2829 (m), 1102 (s), 1051 (s). Mass spectrum: Found 116.04730 Calc. 116.04734 bp. 60-62°C (9mm Hg); 43% isolated yield.

10 ^{1}H NMR ($CDCl_3$) δ 5.19 (dd, J = 6.6, 4.8 Hz, 1 H), 4.68 (d, J = 17.2 Hz, 1 H), 4.4 (d, J = 17.2 Hz, 1 H), 3.52 (s, 3 H), 2.96 (dd, J = 17.0, 6.6 Hz, 1 H), 2.83 (dd, J = 17.0, 4.8 Hz, 1 H) ^{13}C NMR ($CDCl_3$) δ 204.26 (s), 102.37 (d, J = 166 Hz), 79.51 (dd, J = 151, 144 Hz), 55.67 (q, J = 144 Hz), 42.05 (dd, 135, 129 Hz).

11 ^{1}H NMR ($CDCl_3$) δ 6.2 (d, other long range coupling is also evident, J = 10 Hz, 1 H), 6.0 (d, J = 10 Hz, 1 H), 5.35 (bs, 1 H), 4.8 (d, J = 10 Hz, 1 H), 4.30 (dd, J = 10, 3.4 Hz, 1 H), 2.6 (bs, 1 H). ^{13}C NMR ($CDCl_3$) δ 128.25 (d, J = 166 Hz), 124.12 (d, J = 166 Hz), 92.21 (d, J = 162 Hz), 69.07 (t, J = 145 Hz).

12 ^{1}H NMR ($CDCl_3$) δ 4.68 (bs, 1 H), 4.28 (bs, 1 H), 3.12 (d, J = 16 Hz, 1 H), 1.5 - 2.6 (m, 5 H). ^{13}C NMR ($CDCl_3$) δ 204.26 (s), 80.03 (d, J = 156 Hz), 73.67 (d, J = 157 Hz), 43.55 (t, J = 122 Hz), 23.40 (t, J = 127 Hz), 21.53 (t, J = 133 Hz).

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