Singlet Oxygenation of a Conjugated Diallene: Attempt To Prepare a Stable Divinyl Peroxide

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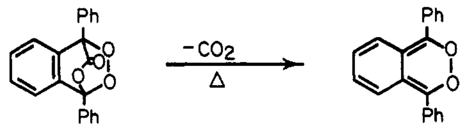
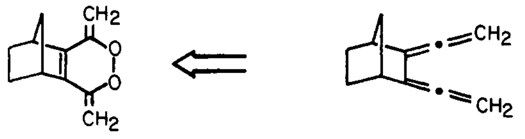
A conjugated diallene, 2,3-divinylidenebicyclo[2.2.1]heptane, was prepared and isolated. Photosensitized oxygenation of this allene leads to two isolated oxygenated products in 50% yield. Detection of these products is interpreted to implicate an unstable cyclic divinyl peroxide intermediate. Attempts to detect this intermediate by low-temperature NMR spectroscopy and by chemiluminescence were unsuccessful. The instability of this compound is attributed to the destabilizing lone-pair interaction of the peroxide oxygen atoms.

Recent advances in the thermal chemistry of organic peroxides have provided further insight into the mechanism of electronically excited state generation and into the processes of chemiluminescence.[1] Part of our continuing interests in this field has been concerned with the identification of new chemiluminescent systems through the synthesis and investigation of novel compounds containing this functional group. The discovery[2] that thermolysis of endoperoxide 1 generates a vinyl peroxide (2) with modest thermal stability (eq 1) prompted us to search for other examples of this type of conjugated, cyclic, unsaturated peroxide.



1 2 (1)

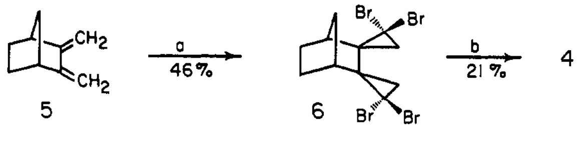
Vinyl peroxides have been implicated as intermediates in several chemical reactions.[3,4] Examples include the cooxidation of phenylacetylene and thiols with molecular oxygen[3] and the cycloaddition of singlet molecular oxygen to conjugated vinyl allenes.[4] We chose as our target molecule compound 3 on the assumption that this divinyl peroxide contains geometric constraints that force the oxygen–oxygen σ bond to be in a plane orthogonal to the molecules π system and that this feature might stabilize this inherently reactive peroxide linkage.[5] Herein we report our attempt to prepare 3 by the cycloaddition of singlet molecular oxygen ($^1O_2$) to conjugated diallene 4.



3 4

Results and Discussion

Scheme I



a) CH_3Br, 50% Aqueous NaOH, (n-butyl)$_3$N, CH_2Cl_2, 50° C, 16 h.

b) LiBr•MeLi, TMEDA, Et_2O, −78° C, 0.5 h.

The synthesis of 4 is illustrated in Scheme I. The starting bicyclic diene 5 is conveniently prepared by the procedure described by Bowe et al.[6] The addition of 2 equiv of dibromocarbene to this compound to give 6 was done by the two-phase method[7] of dihalocarbene generation, using tri-*n*-butylamine[8] as the phase-transfer catalyst. The details of the structural assignment of 6 are presented in the Experimental Section. It is interesting to note, however, that the prediction, based on molecular models, that an anti relationship of the dibromocyclopropyl appendages is preferred in 6 is supported by the asymmetry exhibited by the resonances in the ^1H NMR spectrum and, more notably, in the proton-decoupled ^{13}C NMR spectrum of this compound.

Formation of the diallene is accomplished by treatment of a solution of 6 and tetramethylenediamine in ether at reduced temperature with an excess of lithium bromide complexed methyllithium for 0.5 h.[9] Analysis of the initial mixture from this reaction reveals only one product. However, after a suitable extractive workup at room temperature several products are observed. Chromatography of this mixture on neutral alumina (activity V) with pentane, followed immediately by flash distillation of the appropriate concentrated fraction at reduced pressure, gives the diallene 4 (21%) in greater than 95% purity.[10] The difficulties encountered in the purification of 4 are compounded by the fact that this compound decomposes over several hours at room temperature.[11] Thus, all subsequent reactions of 4 were conducted immediately after completion of its purification. The structure of 4 is consistent with its spectral properties (Experimental Section) and is confirmed by its conversion to adduct 7 with tetracyanoethylene (TCNE; eq 2).

Irradiation (>400 nm) of an oxygen-saturated solution of 4 and tetraphenylporphyrin in carbon disulfide at room

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(9) Skattebøl, L.; Solomon, S. *Org. Synth.* **1969**, *49*, 35 and references therein.

(10) Purity was determined by ^1H NMR integration.

(11) A similar bicyclic diallene prepared previously was also reported to be unstable; see ref 12.

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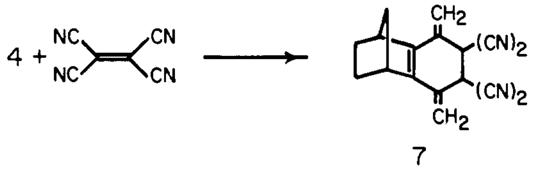
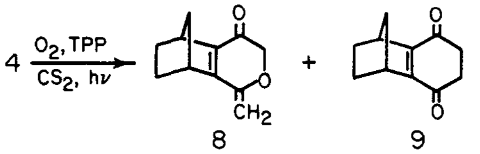


(2)

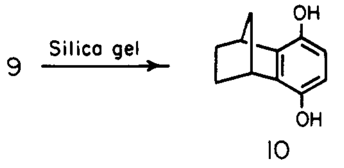
temperature leads to rapid consumption of the diallene as determined by ^{1}H NMR spectroscopy. It is apparent from the spectum that two monomeric products are formed during the dye-sensitized phtooxygenation (eq 3). Neither product survives conventional chromatographic techniques. However, they can be separated and purified by high-performance LC, using a Partisil PAC 10 column at −20 °C.



(3)

The photooxygenation products are identified as keto enol ether **8** (29%) and diketone **9** (21%).[13] In the case of **8**, the ^{1}H NMR spectrum shows two broad singlets correspnding to bridgehead protons at δ 3.10 (1 H) and 3.25 (1 H), which suggest an unsymmetrical bicyclo[2.2.1] structure. Also, vinyl proton absorptions, indicative of enol ethers,[14] are observed at δ 4.5 (1 H, s) and 4.65 (1 H, s). Further, a doublet centered at δ 4.15 (2 H, J = 3 Hz) is noted in the spectrum; this is appropriate for the methylene protons α to both the carbonyl group and the ether linkage.[15] These ^{1}H NMR features, along with appearance of a strong carbonyl absorption at 1675 cm^{-1} [16] in the IR spectrum of **8**, form the basis of the structural assignment of this compound. All of our attempts to isolate **8** from solution were unsuccessful, giving only intractable, presumably polymeric, decomposition products.

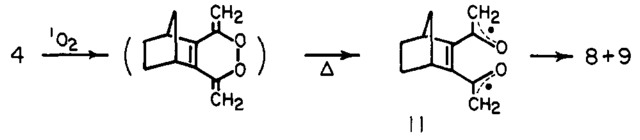
The IR and ^{1}H NMR spectra of **9** are totally consistent with the proposed structure (see the Experimental Section for spectral details). Futher evidence for this structure is obtained by tautomerizing **9** with silica gel to 3,6-dihydroxybenzonorborane (**10**; eq 4). Attempts to isolate untautomerized enedione **9** were unsuccessful.



(4)

To determine the contribution, if any, of a photoinitiated free-radical process[17] to the photooxidation of **4**, the reaction in the presence of a radical initiator was investigated. Thus, irradiation (350 nm) of an oxygen saturated carbon disulfide solution of **4** and *tert*-butyl peroxybenzoate (10 mol %) results in complete consumption of **4** after 45 min. Neither of the two products, **8** or **9**, are detected in this reaction mixture by ^{1}H NMR spectroscopy. This result is consistent with the finding that the yields of **8** and **9** are not affected by inclusion of 3,6-di-*tert*-butyl-4-methylphenol (BHT), a free-radical inhibitor, in the dye-sensitized photooxygenation of **4**. These observations indicate that the disappearance of **4** during the photooxygenation is a result, at least in part, of its reaction with singlet molecular oxygen. Further evidence for this conclusion comes from the observation that diallene **4** quenches the infrared emission of $^1O_2$ in CS_2 solution with a bimolecular rate constant of $(3.3 \times 10^6) \pm (1.3 \times 10^5)$ M^{-1} s^{-1}.

Scheme II



The reactions of $^1O_2$ with conjugated diene systems have been extensively studied and usually give cyclic peroxides.[18] Mechanistically, this reaction is normally viewed as a concerted [4 + 2] cycloaddition. In the present study a similar reaction is proposed and, as seen in Scheme II, is consistent with the formation of **8** and **9**. Thus, cycloaddition of $^1O_2$ to **4** forms the desired divinyl peroxide **3**. However, under the reaction conditions this product evidently is unstable. Cleavage of the peroxide linkage homolytically gives diradical **11**, and intramolecular combination of the radicals logically gives the observed products.

In attempt to increase the stability of **3**, the photooxygenation of **4** was carried out in other solvents ($CDCl_3$, $(CD_3)_2CO$, C_6F_6) and with other sensitizers, all to no avail. Photooxygenation of **4** at −78 °C and analysis by ^{1}H NMR at −60 °C also indicates formation of **8** and **9** with no indication of **3**. Finally, on the assumption that **3** would be chemiluminescent, and with the knowledge that chemiluminescence can be detected at very low levels, we looked for light emission from solutions of **4** photooxygenated at −78 °C and allowed the solutions to warm slowly to room temperature in the presence of an appropriate fluorescer. No light, above a very low background level, was detected in this experiment. Thus, it appears that **3**, if it is indeed formed in the photooxygenation reaction, does not enjoy the hoped for stability.

Conclusion

This investigation has revealed that the diallene **4** reacts rapidly with singlet molecular oxygen. The two monomeric products formed from this reaction are found to have incorporated two oxygen atoms. Although a precursor to these products is not detected, it seems reasonable to assume, after considering the reaction of $^1O_2$ with conjugated diene systems, that a short-lived intermediate does exist and is probably the anticipated divinyl peroxide **3**. The apparent instability of this peroxide is puzzling in comparison to related diacyl peroxides, such as phthaloyl peroxide. A reasonable cause for this difference is that the very strong four-electron repulsive interaction of the oxygen lone pairs in these enforced planar structures is relieved by interaction with the electron-withdrawing carbonyl groups of the diacyl peroxide and cannot be so accommodated by the methylene groups of the vinyl peroxide.

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Experimental Section

General Procedures. Proton magnetic resonance spectra were recorded on a Varian EM-390 spectrometer. A JEOL JNM-FX 60 FT-NMR instrument was used to obtain ^{13}C NMR spectra. Chemical shifts are relative to tetramethylsilane. IR spectra were recorded on either a Perkin-Elmer 237B grating infrared spectrophotometer or a Nicolet 7199 FT-IR instrument. High-performance liquid chromatography (HPLC) was performed on a Perkin-Elmer Series 2 chromatograph equipped with a Perkin-Elmer LC-75 variable-wavelength detector. Mass spectra were obtained with a Varian MAT CH-5 mass spectrometer. Elemental analyses were performed by J. Nemeth and associates, Department of Chemistry, University of Illinois, Urbana, IL. Melting points were determined on a Büchi apparatus by the capillary method and are uncorrected.

Materials. All reaction solvents were either spectroscopy grade or were purified by standard techniques. The hexane (Burdick and Jackson distilled in glass) used in preparative HPLC was purified by washing successively with concentrated sulfuric acid, water, and a saturated aqueous solution of sodium carbonate. It was then dried (calcium chloride), passed through a basic alumina column (activity I), and then distilled.

2,3-Dimethylenebicyclo[2.2.1]heptane (5) was prepared by the method of Bowe et al.[6] except that diimide[19] was used to reduce 5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene.

***dl*-2′,2′,2″,2″-Tetrabromodispiro[bicyclo[2.2.1]heptane-2,1′-cyclopropane-3′,1″-cyclopropane] (6).** A two-phase mixture consisting of diene **5** (5.0 g, 4.2×10^{-2} mol), methylene chloride (100 mL), bromoform (84.6 g, 0.334 mol), 50% aqueous sodium hydroxide (150 mL), and tri-*n*-butylamine (100 mL) was vigorously stirred by a mechanical stirrer for 16 h at 50 °C under a nitrogen atmosphere. The crude reaction mixture was diluted with methylene chloride (200 mL) and this organic solution was washed successively with water (3 × 100 mL), 10% aqueous hydrochloric acid (3 × 100 mL), and water (2 × 100 mL). The organic layer was dried ($MgSO_4$) and the solvent removed by rotary evaporation. The dark-brown crude material obtained was flushed through silica gel with hexane. This hexane solution was concentrated by rotary evaporation and the residue was subjected to vacuum distillation to remove the excess bromoform. The pot residue was cooled to −20 °C, whereupon the viscous oil solidified. This crude crystalline material was recrystallized from ethanol/pentane to afford 9.1 g (46%) of white crystals: mp 117–118 °C; ^1H NMR ($CDCl_3$) δ 1.0–2.1 (8 H, m), 2.2 (1 H, br s), 2.7 (1 H, br s), 3.1–3.7 (2 H, AB, $\delta_A = 3.12$, $\delta_B = 3.61$, $J_{AB} = 9$ Hz); ^{13}C NMR ($CDCl_3$) δ 25.8, 26.1, 27.5, 28.6, 34.1, 36.5, 37.7, 41.4, 41.7, 53.2, 54.05. Anal. Calcd for $C_{11}H_{12}Br_4$: C, 28.48; H, 2.61; Br, 68.91. Found: C, 28.67; H, 2.45; Br, 69.06.

2,3-Divinylidenebicyclo[2.2.1]heptane (4). To a magnetically stirred diethyl ether solution (15 mL) of the tetrabromide **6** (0.50 g, 1.08×10^{-3} mol) and tetramethylethylenediamine (10 μL) under a nitrogen atmosphere and cooled to −78 °C was added dropwise a diethyl ether solution of lithium bromide complexed methyl lithium (8.6 mL, 4.32×10^{-3} mol). The reaction mixture was stirred at −78 °C for 30 min and then methanol (0.5 mL) was added and the resulting solution was warmed to room temperature, diluted with ether (100 mL), extracted with ice water (3 × 30 mL), and dried (K_2CO_3). The solvent was removed by rotary evaporation and the residue was passed quickly through an alumina column (neutral, activity V, 15 g) using pentane as the elutant. The yellowish oil obtained after removal of the solvent (0.10 g, 64%) was found by ^1H NMR spectroscopy to be mostly the desired diallene **4**. Purification was accomplished by flash distillation at room temperature under reduced pressure ($<10^{-4}$ torr), using a sublimation apparatus in which the cold finger was cooled to liquid nitrogen temperature. The colorless oil (32×10^{-3} g, 21%) has the following spectral characteristics: ^1H NMR (CCl_4) δ 1.0–2.0 (8 H, m), 2.9 (2 H, br s), 4.8 (4 H, s); IR (film) 1960 (m), 850 (m) cm^{-1}; MS (70 eV), *m/e* (relative intensity) 144 (M^+, 37), 128 (33), 117 (41), 116 (37), 115 (100), 91 (36).

TCNE Adduct of Compound 4. A carbon tetrachloride solution (5 mL) of **4** (3.4×10^{-2} g, 2.36×10^{-4} mol) and tetracyanoethylene (2.7×10^{-2} g, 2.1×10^{-4} mol) was stirred at room temperature under nitrogen for 6 h. The solvent was removed by rotary evaporation and the residue was purified by preparative HPLC (3% isopropyl alcohol/hexane, Perkin-Elmer silica A, 10-μm paticle size, 9 mm × 25 cm) to afford adduct **7**: 21.2×10^{-3} g, 37%; ^1H NMR (CCl_4) δ 1.0–2.0 (6 H, m), 3.2 (2 H, br s), 5.7–5.9 (4 H, AB, $\delta_A = 5.7$, $\delta_B = 6.1$, $J_{AB} = 3$ Hz); exact mass calcd for $C_{17}H_{12}N_4$ 272.1062, found 272.1064.

General Procedure for the Dye-Sensitized Photooxygenation of 4. A solution of **4** (24×10^{-3} g, 1.66×10^{-4} mol) and tetraphenylporphyrin (2×10^{-3} g) in carbon disulfide (30 mL) was saturated with oxygen and then maintained under an oxygen atmosphere while being irradiated with the output of a 250-W tungsten–halogen lamp filtered through a Corning CS3-73 glass plate (>400 nm) for 4 min at room temperature. The solvent was removed to give the crude product. Product yeilds were obtained by dissolving the crude product and chloroform (internal standard) in carbon disulfide (1 mL) and integrating the appropriate peaks in the ^1H NMR spectrum (**9**, 21%; **8**, 29%). Compounds **8** and **9** were separated by HPLC on a Whatman Partisil PAC-10 column (9 mm i.d. × 50 cm) using 8% isopropyl alcohol/hexane as the elutant. The column was housed in a glass jacket and was cooled to −20 °C by means of a recirculating bath. The products were monitored at 270 nm by UV (**8**, $V_{R'} = 37$ mL; **9**, $V_{R'} = 72$ mL).

Compound **8** has the following spectral properties: ^1H NMR (CS_2) δ 1.0–2.0 (7 H, m), 3.1 (1 H, br s), 3.25 (1 H, br s), 4.15 (2 H, d, $J = 3$ Hz), 4.5 (1 H, s), 4.65 (1 H, s); IR (CS_2) 2964 (m), 2866 (m), 1675 (s), 1102 (m) cm^{-1}.

Compound **9** has the following spectral characteristics: ^1H NMR (CS_2) δ 1.0–2.0 (6 H, m), 2.7 (4 H, m), 3.35 (2 H, br s); IR (CS_2) 2964 (m), 2873 (m), 1676 (s) cm^{-1}. A sample of this material was stirred at room temperature with silica gel (1 g) in diethyl ether (5 mL) for 5 min. Filtration of the solution followed by removal of the solvent by rotary evaporation gives 3,6-dihydroxybenzonorborane (**10**), identified by comparison with an authentic sample (Chemalog).

Photolysis of 4 and *tert*-Butyl Peroxybenzoate. Under an oxygen atmosphere a solution of **4** (21×10^{-3} g, 1.46×10^{-4} mol) and *tert*-butyl peroxybenzoate (3 mg, 10 mol%) in carbon disulfide (1 mL) was irradiated in a Rayonet instrument (350 nm) unitl it was determined by ^1H NMR that all of the diallene was consumed (75 min). No resonances were observed in the region between δ 3.0 and 5.0 (complex multiplet seen in methylene region) in the ^1H NMR spectrum of the reaction product.

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Registry No. **3**, 84602-29-9; **4**, 84602-30-2; **5**, 36439-78-8; **6**, 84602-31-3; **7**, 84602-32-4; **8**, 84602-33-5; **9**, 84602-34-6; **10**, 16144-91-5; 5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene, 84602-35-7.

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