ium salts, **4** and **5**. Increased electron density on carbon-1 for analogs of **8** was found by CNDO/2 calculations, which is in complete agreement with the carbon chemical shifts.[7] The decreased shielding of carbon-1 in the conjugated enamine **8** compared to **4** or **5** is undoubtedly a consequence of delocalization of the charge into the acetyl group in **8**. It should be noted that carbon-1 in the 2-ethoxyvinyltriphenylphosphonium bromide (**6**) is deshielded by 18.8–15.7 ppm compared to the carbon-1 resonances for **4** and **5**. This is consistent with the notion that delocalization into a π system becomes increasingly inhibited when the atom possessing the unshared pair of electrons becomes more electronegative. That carbon-1 in **6** is shielded by 8.1 ppm from carbon-1 in ethoxyethane (**9**) is probably a result of the combined electronic changes induced into the π system by the substitution of the additional methyl group in **6** and steric differences between **6** and **9**. It should be noted at this point that the accumulation of electron density on carbon-1 for **4** and **5** does not rule out the intervention of resonance structure **1c**, since the diffuseness of the d orbitals[2] will still leave most of the electron density concentrated near carbon-1.

The hydrazone substituted methylenetriphenylphosphonium salt, **7**, a tautomer of the enaminophosphonium salts, **4** and **5**, exhibits no unusual behavior when comparing the ^{13}C chemical shifts and $^{13}C-^{31}P$ couplings to simple saturated phosphonium salts.[1] It is seen in Table II that the coupling of phosphorus to carbon-1 increases from 53.7 Hz in **7** to 89.4 Hz in **3**. This increase is typical on going from an sp^3 to an sp^2 hybridized carbon as described previously.[1] The β-amino vinyl substituted phosphonium salts have a $^1J(^{31}P-^{13}C)$ which is 30.8 Hz larger for carbon-1 than their equivalently hybridized analog, **3**. However, the electron density on carbon-1 is increased in **4** and **5** compared to **3** and if effective nuclear charge considerations[8] are valid in this situation, there should be a decrease in the magnitude of $^1J(^{31}P-^{13}C)$. A similar dramatic increase in $^1J_{P-C}$ was found on going from a phosphonium salt to a ylide.[1,9] It was rationalized[1] that this is a consequence of electron density being transfered from the carbon bearing the formal negative charge to phosphorus, presumably via d orbitals. Therefore, the inclusion of resonance structure **1c** should cause $^1J(^{31}P-^{13}C)$ for carbon-1 to increase. This infers that electron density on C-1 is being transferred to a greater extent onto phosphorus in **4** and **5** than in **3**. In keeping with this argument the slightly increased $^1J(^{31}P-^{13}C)$ coupling of carbon-1 of **6** compared to **3** (ΔHz = 7.0) is justified, since the contribution of **1b** is diminished for **6** owing to the greater electronegativity of oxygen (the contribution of **1c** must also diminish).

Further evidence for the contribution of resonance structure **1c** is given by the slight, but definite, decrease in the shielding of the C-1 phenyl carbons in **4** and **6** compared to **3** (3.2 and 1.5 ppm, respectively). This effect was also noted in going from a phosphonium salt to an ylide, albeit the differences were greater (11.5–15.9 ppm)[1].

The extent of hyperconjugative interaction of the methyl group in **3** is difficult to ascertain. Comparison of $^1J(^{31}P-^{13}C)$ of carbon-1 in **3** vs. vinyltriphenylphosphonium bromide reveals an increase of only 9.1 Hz;[1] however, steric differences are also likely to make changes in the magnitude of the coupling. Thus, the additional contribution of resonance structure **1c** for **3** by hyperconjugation must be small.

The electronic description of β-amino and alkoxyvinylphosphonium salts presented here is intriguing. These compounds, by virtue of the delocalization of electrons on nitrogen or oxygen onto d orbitals on phosphorus, seem to represent, electronically, a median between a "normal" phosphonium salt and a carbon-phosphorus ylide. An examination of the synthetic utility of these compounds is under active investigation.

Experimental Section

Spectra were obtained on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. The ^{13}C data were taken at an operating frequency of 22.63 MHz. The ^{13}C chemical shifts are reported as referenced to internal Me_4Si. All samples were run in approximately 0.05 *M* solutions of $CDCl_3$ or DMSO-d_6 (as indicated in footnote *a*, Table I) at 28° with broad band ^1H decoupling. The preparation of the phosphonium salts will be reported elsewhere.

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Photosensitized Oxygenation of *trans,trans*-1-Methylcyclodeca-1,6-diene. A Regiospecific Hydroperoxidation with Singlet Oxygen

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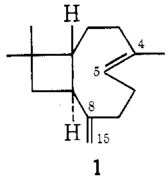
The reactive species of dye-sensitized photooxygenation is presumably singlet oxygen,[1] which is known to react with olefins and conjugated dienes in three ways, namely "ene" reaction, Diels–Alder reaction, and 1,2-dioxetane formation.[1,2] In principle, nonconjugated dienes can react with singlet oxygen to give either the transannular cycloaddition product when the geometry is favorable[3] or the "ene" products, a mixture of allylic hydroperoxides.[2]

The hydroperoxidation of olefins with singlet oxygen is an important synthetic method for the preparation of allylic hydroperoxides and allylic alcohols. Although this hydroperoxidation is generally believed to occur faster with tri- and tetrasubstituted olefins than with di- or monosubstituted ones, there are only a few literature reports in which a completely regiospecific hydroperoxidation of a double bond was actually observed within the molecule.[4]

(−)-Caryophyllene (**1**) was reported to react with singlet



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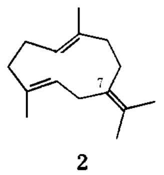

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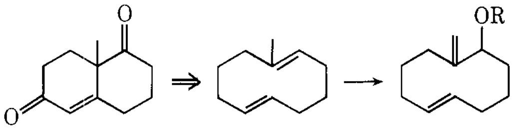
oxygen at the trisubstituted double bond (C-4,5) faster than at the exocyclic double bond (C-8,15), thus exclusively generating 4-methylene-5-hydroperoxy derivative.[4a] Germacrene (**2**) was reported to react with singlet oxygen at the isopropylidene double bond much faster than the endocyclic double bonds, giving specifically the 7-hydroperoxy derivative.[4b]

We have studied the dye-sensitized photooxygenation of *trans,trans*-1-methylcyclodeca-1,6-diene (**4**), because it has two transannularly interacting double bonds which are suitable for a cycloaddition reaction, and because the two double bonds have different substitution patterns which are capable of revealing the regiospecificity of the "ene" reaction. The diene **4** was readily synthesized from 9-methyloctalin-1,6-dione (**3**) according to literature procedures.[5] A methanol solution of **4** was irradiated in the presence of Methylene Blue at 10° for 4.5 hr while pure oxygen was bubbled through. The disappearance of **4** was monitored by taking aliquots and analyzing them on TLC. A single produce **5a** isolated in 55% yield showed a positive peroxide test with starch–iodine and gave an alcohol **5b** upon reduction with aqueous methanolic sodium sulfite.



3 4 5a, R = OH
b, R = H

Analysis by TLC, GC, and NMR spectrum clearly indicated that alcohol **5b** was homogenous and free from other possible isomers. A thorough search for the transannular cycloaddition products proved futile. It is interesting to note that the hydroperoxidation is completely regiospecific in spite of the fact that four other positions are also available for the "ene" reaction. A qualitative reactivity order of the double bonds toward the singlet oxygen "ene" reaction appears to be the following: isopropylidene > endocyclic trisubstituted olefin > endocyclic disubstituted olefin > isopropenyl > *exo*-methylene.[4] Although there is no straightforward explanation for the exclusive formation of the *exo*-methylene *sec*-hydroperoxide over the other possible endocyclic *tert*-hydroperoxide products, the observed regiospecificity should be of considerable value in synthetic design.[6]

Experimental Section

The NMR spectra were recorded on a Jeol JNM-MH 100 spectrometer. Ir spectra were recorded on a Perkin-Elmer Model 421 grating spectrophotometer. Mass spectral data were obtained on a Hitachi RMU-6 spectrometer. Gas chromatograms were run on a Varian Model 2700 using the columns 5 ft × 0.125 in, 10% OV-101 on Anakrom C.D. and 5 ft × 0.125 in, 10% FFAP on Anakrom C.D. Microanalysis was performed by Dr. R. C. Rittner at Olin Laboratory, New Haven, Conn.

***trans,trans*-1-Methylcyclodeca-1,6-diene (4)** was prepared from 1-methyloctalin-1,6 dione (**3**)[7] according to literature procedures[5] in ca. 35% overall yield: NMR ($CDCl_3$) δ 1.0–2.0 (m, 4 H), 1.64 (s, 3 H), 2.0–2.6 (m, 8 H), 5.0–5.5 (m, 3 H).

2-Methylenecyclodeca-*trans*-6,7-enol (5b). A solution of diene **4** (266 mg, 1.77 mmol) and Methylene Blue (10 mg) in methanol (20 ml) at 10° was irradiated with a 275-W sun lamp while pure oxygen was bubbled through the solution. After 4.5 hr, the solution was poured into cold water and extracted with ether. The extract was washed thoroughly with water, dried (Na_2SO_4), and evaporated at room temperature to give crude hydroperoxide **5a**. Pure **5a** (oil, 180 mg, 55% yield) was obtained by a thick layer chromatography (2 mm SiO_2, developed in 40% ether in hexane): NMR ($CDCl_3$) δ 1.0–2.4 (m, 12 H), 4.36 (br, 1 H), 5.18 (s, 1 H), 5.28 (s, 1 H), 5.42 (m, 2 H).

Stirring a solution of **5a** in methanol (20 ml) and 10% sodium sulfite in water (20 ml) for 5 hr at room temperature, followed by an extractive work-up with ether, gave pure alcohol **5b** in quantitative yield: oil, homogeneous by TLC (SiO_2) and GC (OV 101, 140°); ir 3600, 3080, 3030, 1640, 1448, 1345, 980, 910 cm^{-1}; NMR ($CDCl_3$) δ 1.0–2.4 (m, 12 H), 4.08 (br, 1 H), 4.98 (s, 1 H) 5.18 (s, 1 H), 5.36 (m, 2 H); MS *m/e* 166 (M^+), 148, 134, 124, 120.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.52; H, 10.84. Found: C, 79.33; H, 10.77

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Registry No.—**3**, 20007-72-1; **4**, 13304-33-1; **5a**, 54814-44-7; **5b**, 54814-45-8.

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(7) Purchased from Aldrich Chemical Co.

Synthesis of Three Substituted Aminochloropropanes

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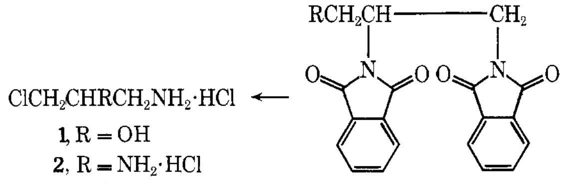
In the course of a study of male antifertility agents it became necessary to synthesize several aminochloropropanes. Because of the proximity of mutually interactive functional groups in such molecules, the instability of the products was a problem that had to be overcome. One of these, 1-amino-3-chloro-2-propanol hydrochloride (**1**), had very interesting properties and its pharmacology has been reported elsewhere.[1,2]

The synthesis of 1,2-diamino-3-chloropropane dihydrochloride (**2**) has been reported by Philippi[3] via the following sequence. 2,3-Dibromopropanol on fusion with potassium phthalimide gave 2,3-bisphthalimidopropanol (**3**).



$ClCH_2CHRCH_2NH_2 \cdot HCl$
1, R = OH
2, R = $NH_2 \cdot HCl$

3, R = OH
4, R = Cl

Phosphorus pentachloride converted **3** to **4**, which gave **2** on hydrolysis. Although part of the sequence has been repeated in the literature[4] but without proof of structure of the products, in our hands dehydrobromination occurred on the first step, yielding phthalimide and potassium bro-