References and Notes

(1) Cis and trans designations are in accordance with *Chemical Abstracts* usage by which, for example, the cis isomer has the senior groups (as defined by the sequence rule) on the same side of the reference plane of the ring: cf. *Chem. Abstr.*, **76**, 85 I (1972); *J. Chem. Inf. Comput. Sci.*, **15**, 67 (1975).
(2) K. L. Marsi, *J. Org. Chem.*, **40**, 1779 (1975).
(3) (a) K. L. Marsi, J. L. Jasperse, F. M. Llort, and D. B. Kanne, *J. Org. Chem.*, **42**, 1306 (1977). (b) The pseudo-first-order rate constants for *cis*- and *trans*-**4** for the inversion component of benzyl cleavage at phosphorus are, respectively, 0.96×10^{-3} and 1.16×10^{-3} s^{-1} at 80.0 °C in 1.28 N NaOH (50% aqueous ethanol) (ref 3a).
(4) Personal communication from K. D. Berlin and D. van der Helm.
(5) R. Luckenbach, *Z. Naturforsch. B*, **31**, 1127 (1976); R. Luckenbach, *Phosphorus*, **3**, 117 (1973), and references contained therein.
(6) K. L. Marsi and R. T. Clark, *J. Am. Chem. Soc.*, **92**, 3791 (1970); K. L. Marsi, *J. Org. Chem.*, **40**, 1779 (1975); ref 3a.
(7) Stereochemical relationships among 4-*tert*-butylphosphorinane derivatives mentioned in this paper were established previously (see ref 3a).

Atomic Oxygen. 8. Reactions of Methylenecycloalkanes with Oxygen (^{3}P) Atoms

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The reactions of atomic oxygen with unsaturated organic compounds have demonstrated that the primary reactive intermediates can undergo extensive rearrangement before forming isolable oxygenated products. The examination of the product mixture allows one to determine two important factors of the reaction: the orientation of the oxygen atom addition to the molecule and the relative migratory aptitudes of substituents on the molecule's unsaturated site. The reactions of methylenecycloalkanes with O(^{3}P) illustrate the effects of ring size and strain on the former of these two factors.

In this study, conditions for the gas-phase production and reaction of atomic oxygen were derived from the pioneering work of Cvetanovic and co-workers.[2] Ground-state (^{3}P) oxygen atoms were produced by the mercury photosensitized decomposition of nitrous oxide.[3] The reaction apparatus and conditions have been described previously.[4] The total pressure before photolysis was 0.9 atm, and the reaction temperature was 25–30 °C.

The products of the reactions of methylenecycloalkanes (**1**) with atomic oxygen consisted of spiro epoxides (**2**), cycloalkanecarboxaldehydes (**3**), cycloalkanones (**4**), and alken-2-ones (**5**). Product yields are listed in Table I. A probable mechanism for the formation of these products is shown in Scheme I.

Several features of this mechanism are of interest. Previous research has shown that triplet oxygen atoms add to olefins to produce carbon–oxygen 1,3-biradicals. In the case of an unsymmetrical olefin, the orientation of addition parallels that obtained when a monoradical adds to the olefin. The direction of addition is controlled by radical stability. In the reactions of methylenecycloalkanes, the orientation of addition is approximately indicated by the ratio of aldehydic product **3** to ketonic products **4** and **5**. These ratios in the series of methylenecyclobutane (2.9), methylenecyclopentane (4.6), and methylenecyclohexane (21) demonstrate that increasing the ring size increases the stability of the cycloalkyl radical site (intermediate **6**) relative to the stability of the methylene radical (intermediate **7**).[5]

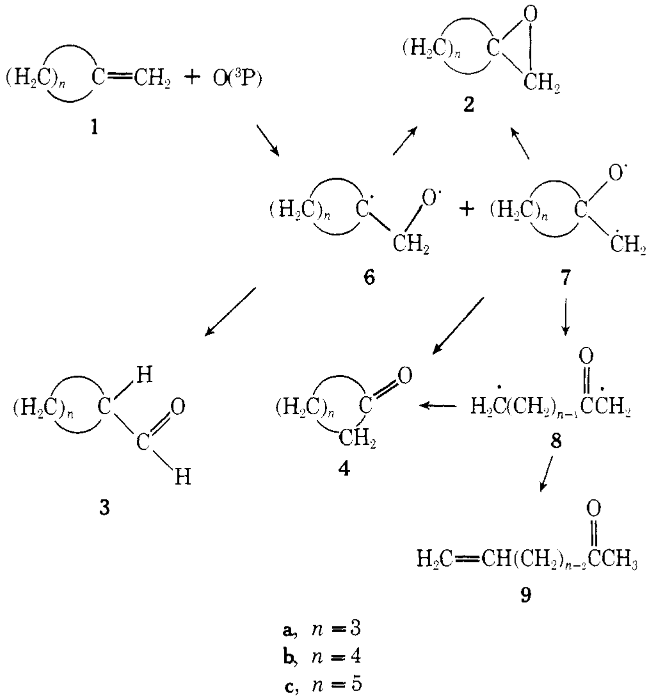
Another aspect of the proposed mechanism is the ring opening of 1,3-biradical **7** to yield the 1,ω-biradical **8**. It has been noted in previous atomic oxygen studies[6,7] that the rearrangement of alkyl radicals is partially accomplished by detachment of the migrating radical from the remainder of the molecule. In acyclic olefins, these detached alkyl radicals can be scavenged by added molecular oxygen. The formation of biradical **8** is analogous to this process.

Table I. Product Yields[a] from Reactions of O(^{3}P) with Methylenecycloalkanes

Reactant	Product yield, % 2	3	4	5
1a ($n = 3$)	35	29	7.1	2.9
1b ($n = 4$)	57	19	2.6	1.5
1c ($n = 5$)	56	26	0.81	0.40

[a] Product yields are based on the measured amounts of nitrogen produced by the mercury photosensitized decomposition of nitrous oxide. Reproducibility among reactions was ±10% of the stated yields.

Scheme I



Relative rate constants for the reactions of the methylenecycloalkanes were also determined. These rates (relative to 2-methylpropene as 1.00) were: methylenecyclobutane, 1.05; methylenecyclopentane, 1.81; and methylenecyclohexane, 0.99. The same reactivity pattern has been observed for the addition of dichlorocarbene to these olefins,[8] but the origin of the enhanced reactivity of methylenecyclopentane is not clear.

Experimental Section

Reaction Technique. Procedures for the reaction of atomic oxygen with organic substrates have been described previously.[4] The olefins used were obtained from Chemical Samples Co. and were determined to be of >99% purity. Analyses of unreacted olefins recovered after photolysis showed that the reactant was not isomerized under the reaction and workup conditions used. The reaction of methylenecyclopropane with O(^{3}P) was attempted several times, but this substrate polymerized rapidly under the reaction conditions.

Relative rate constants of the methylenecycloalkanes vs. cyclopentene were determined by the method of Cvetanovic[2] and converted to the usual standard, 2-methylpropene, using the figure $k_{\text{cyclopentene}}/k_{\text{2-methylpropene}} = 1.19$. Reaction temperature during these studies was controlled at 24 ± 2 °C.

Product Analysis. Products of the reaction of **1a** were analyzed by VPC on a dinonyl phthalate column at 99 °C. Product mixtures from **1b** and **1c** were analyzed on an XE-60 column at 132 and 155 °C, respectively.

Authentic samples of all products were available for comparative VPC retention times and, where possible, comparative NMR, IR, and

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mass spectra. The cycloalkanones **4**, cyclohexanecarboxaldehyde (**3c**), and 5-hexene-2-one (**5b**) were obtained commercially. 4-Penten-2-one (**5a**) was available as a major impurity in 3-penten-2-one obtained from the Aldrich Chemical Co. Authentic samples of cyclobutanecarboxaldehyde (**3a**) and cyclopentanecarboxaldehyde (**3b**) were obtained from the reactions of cyclopentene and cyclohexene with oxygen atoms. Spiro epoxides **2** were prepared by reaction of the olefins with *m*-chloroperbenzoic acid. 6-Hepten-2-one (**5c**) was made by the acetoacetic ester synthesis.[9]

Trace amounts of 2-methylenetetrahydrofuran and 2-methylenetetrahydropyran were detected from the reactions of **1a** and **1b**, respectively. These enol ethers were independently synthesized by dehydrohalogenation reactions.[10]

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Registry No.—**1a**, 1120-56-5; **1b**, 1528-30-9; **1c**, 1192-37-6; **2a**, 157-48-2; **2b**, 185-60-4; **2c**, 185-70-6; **3a**, 2987-17-9; **3b**, 872-53-7; **3c**, 2043-61-0; **4a**, 120-92-3; **4b**, 108-94-1; **4c**, 502-42-1; **5a**, 13891-87-7; **5b**, 109-49-9; **5c**, 21889-88-3.

Reference and Notes

(1) (a) Present address: Department of Chemistry, The Pennsylvania State University, University Park, Pa. 16802. (b) Part VII: J. J. Havel and K. H. Chan, *J. Org. Chem.*, **42**, 569 (1977).
(2) R. J. Cvetanovic, *Adv. Photochem.*, **1**, 115 (1963).
(3) R. J. Cvetanovic, *J. Phys. Chem.*, **75**, 3056 (1971).
(4) J. J. Havel, *J. Am. Chem. Soc.*, **96**, 530 (1974).
(5) These figures are based on the assumption that the rates of ring closure of intermediates **6** and **7** to form epoxide **2** are nearly equal. This has not been rigorously proven; however, the assumption is reasonable, since the fast ring closure is preceded by a slow triplet to singlet spin inversion. This spin inversion should proceed at equivalent rates for intermediates **6** and **7**.
(6) R. J. Cvetanovic, *Can. J. Chem.*, **36**, 623 (1958).
(7) J. J. Havel and K. H. Chan, *J. Am. Chem. Soc.*, **97**, 5800 (1975).
(8) E. V. Couch and J. A. Landgrebe, *J. Org. Chem.*, **40**, 1636 (1975).
(9) M. Matsui, T. Yamaguchi, T. Kato, and G. Funazo, *Bull. Chem. Soc. Jpn.*, **26**, 194 (1953).
(10) A. Kankaanpera, E. Taskinen, and P. Salomaa, *Acta Chem. Scand.*, **21**, 2487 (1967); J. Cologne and P. Lasfargues, *Bull. Soc. Chim. Fr.*, 177 (1962).

Position of Nucleophilic Attack on Propargylic ↔ Allenylic Cations. An Ab Initio Molecular Orbital Calculation

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In an earlier communication,[1] we reported on the mechanism of addition of HCl to 1,2,3-pentatriene in ethanol-water (95% v/v). The first and rate-determining step is a proton transfer to the terminal carbon atom. In the second step, a chloride ion is attached to the intermediate cation to give 20% allenylic chloride (1,2 adduct) and 80% propargylic chloride (1,4 adduct). In sulfolane–CH_2Cl_2 (80:20 v/v), this ratio is 50:50.

$$\mathrm{CH_3{-}C^4H{=}C^3{=}C^2{=}C^1H_2 + H^+ \xrightarrow{slow} [CH_3{-}C_\alpha{}^4H\overset{\cdots}{-}C^3\overset{\cdots}{\equiv}C_\beta{}^2{-}C^1H_3]^+}$$

$$\mathrm{[CH_3{-}C_\alpha{}^4H\overset{\cdots}{-}C^3\overset{\cdots}{\equiv}C_\beta{}^2{-}C^1H_3]^+ + Cl^- \rightarrow CH_3CH{=}C{=}CClCH_3 + CH_3CHClC{\equiv}CCH_3}$$

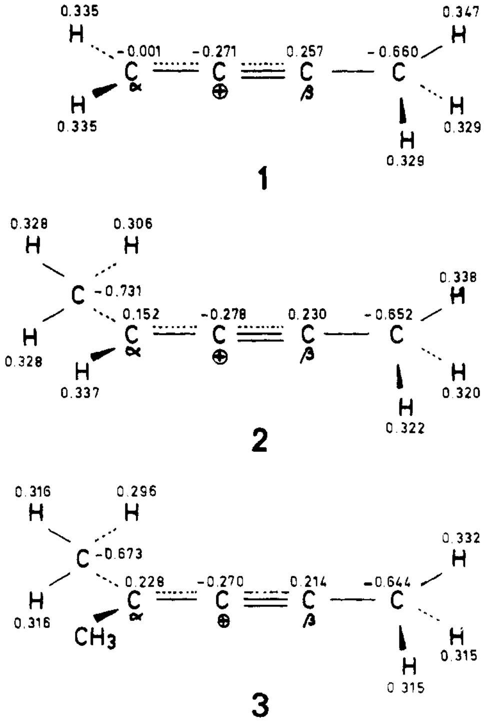

Figure 1. Net atomic charges from ab initio wave functions.

Similar intermediate carbocations are generated by S_N1 solvolysis of allenylic or propargylic halides or tosylates in aqueous solvents.[2–8] In these solvolysis reactions attack on the cation by solvent occurs exclusively at C_α to give propargylic products, unless attack at C_α is sterically hindered. The high preference for attack at C_α rather than at C_β is not expected on the basis of ^1H[9] and ^{13}C NMR[10] measurements on the relevant cations. These measurements suggest that the positive charge is present not exclusively on the propargylic position but, to a certain extent, also on the allenylic position.

In order to better understand the behavior of these cations as well as the possible influence of methyl substituents, we calculated ab initio charge distributions and molecular electrostatic potentials for cations **1–3**. A (C 6s,3p/H 3s) basis set of Gaussian-type functions contracted to a split-valence [3s,2p/2s] set was adopted.[11] Geometries of the cations were taken from ref 12–14. Gross atomic populations were calculated from the wave functions by means of Mulliken's population analysis.[15]

$$\left[\mathrm{C_\alpha{}^4H_2\overset{\cdots}{-}C^3\overset{\cdots}{\equiv}C_\beta{}^2{-}C^1H_3}\right]^+ \quad \mathbf{1}$$

$$\left[\mathrm{CH_3{-}C_\alpha{}^4H\overset{\cdots}{-}C^3\overset{\cdots}{\equiv}C_\beta{}^2{-}C^1H_3}\right]^+ \quad \mathbf{2}$$

$$\left[\mathrm{(CH_3)_2C_\alpha{}^4\overset{\cdots}{-}C^3\overset{\cdots}{\equiv}C_\beta{}^2{-}C^1H_3}\right]^+ \quad \mathbf{3}$$

The corresponding net atomic charges (in units of proton charge) are given in Figure 1. It appears that cations **1** and **2** have a higher positive charge on C_β than on C_α. However, the atomic charges on C_β and C_α are not the only determining factors for nucleophilic attack. One should also include the charge distributed over the hydrogen atoms. Therefore, we have calculated the total charge on each side of the central carbon atom C^3. (The charge on C^3 is approximately equal for the three cations.) The results are given in Table I, where q_{prop} is the total charge on the atoms to the left of C^3 and q_{all} is the total charge on the right-hand side (cf. Figure 1).

In all cations, $q_{\mathrm{prop}} > q_{\mathrm{all}}$, i.e. most of the positive charge is associated with the propargylic center. Moreover, the ratio

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