

- (3) M. E. Jung and T. J. Shaw, *J. Amer. Chem. Soc.*, **102**, 6304 (1980).
- (4) J. S. Brimacombe, H. W. Murray and Z. Haque, *Carbohydr. Res.*, **45**, 45 (1975).
- (5) Takeda Chemical Industries, Ltd. Jpn. Kokai Tokyo Koho JP 57, 140, 789 (82, 140, 789).
- (6) E. A. Ford and P. M. Ruoff, *Chem. Commun.*, 630 (1965).
- (7) R. O. Mumma, A. J. Verlangieri and W. W. Weber, II, *Carbohydr. Res.*, **19**, 127 (1971).
- (8) The compound **2a** was purified by a preparative TLC of silica gel (ether-ethanol, 4:1 containing a small amount of triethylamine) to afford yellow syrup, R_f 0.24 (ether).
- (9) The analytical sample of compound **2b** was purified by a preparative TLC of silica gel (ether) to afford a pale yellow syrup, R_f 0.60 (ether); IR (neat) ν_{\max} : 1780, 1750, 1675 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ : 2.01 (6H, s, 2 acetate Me), 4.23—4.90 (7H, m, H-5, H-6, allylic H), 5.18 (1H, d, $J=3.5\text{Hz}$, H-4), 5.22–5.47 (4H, m, terminal vinylic H), 5.70–6.27 (2H, m, vinylic H). *Anal.* calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_8$: C 56.47, H 5.92; found: C 56.32, H 6.39.
- (10) The compound **3a** was prepared using the method of Jackson-Jones (Ref. 2b and 3).
- (11) The product mixture was fractionated on a column of silica gel (hexane-ethyl acetate, 7:3) to afford pure **3b** as a colorless syrup, R_f 0.24 (hexane-ethyl acetate, 8:2); IR (neat) ν_{\max} : 1785, 1750, 1670 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ : 1.38 (6H, s, isopropylidene Me), 3.97–5.03 (7H, m, H-5, H-6, allylic H), 5.20 (1H, d, $J=3.5\text{ Hz}$, H-4), 5.22–5.50 (4H, m, terminal vinylic H), 5.65–6.25 (2H, m, vinylic H). *Anal.* calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_6$: C 60.80, H 6.80; found: C 59.96, H 6.89.
- (12) K. S. Kim and W. A. Szarek, *Carbohydr. Res.*, **67**, C13 (1978).

Reactivity of 1,1-Diphenyl-2-vinylcyclopropane to Singlet Oxygen

Sang Chul Shim[†] and Jeong Sup Song

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea

(Received August 17, 1984)

In many ways the chemical properties of the cyclopropane ring resemble those of the carbon-carbon double bond. Cyclopropane compounds have been found to undergo addition reactions with electrophilic, nucleophilic and radical reagents.^{1,2} Vinylcyclopropane compounds which exhibit bifunctionality, a vinyl group and a cyclopropyl ring, show much enhanced chemical reactivities and the homodienyl vinylcyclopropanes show extension of conjugative effects from the unsaturated double bond to the cyclopropane ring. As a result, in certain chemical reactions the double bond could be transmitted and the cyclopropane ring could be opened more readily.³ However, cyclopropane compounds have aroused many controversial problems such as ring strains, ring structures, transmission of resonance effects, classical or nonclassical nature of cyclopropyl carbinyl species (cation, anion and radical), *etc.* Especially, there has been long standing controversies concerning the ability of cyclopropane ring to extend or transmit conjugation and its geometrical requirements, if any, for conjugation.^{4,5}

For this reason, we undertook the study of the dye-sensitized photooxygenation of 1,1-diphenyl-2-vinylcyclopropane (VCP-DPh) and compared the results with those of previous observations.⁶

Dye-sensitized photooxygenation of 1,1-diphenyl-2-vinylcyclopropane (VCP-DPh) was carried out in pure acetone solution with $8 \times 10^{-3} M$ VCP-DPh and $2 \times 10^{-6} M$ Rose Bengal. The solution was irradiated at 10°C under oxygen with a 300-W sun lamp. The substrate was also

irradiated with benzophenone sensitizer at 366 nm under oxygen. However, VCP-DPh was stable to singlet oxygen and the expected photoene product (cyclopropylidene derivative) or cycloaddition to vinyl group was not observed.

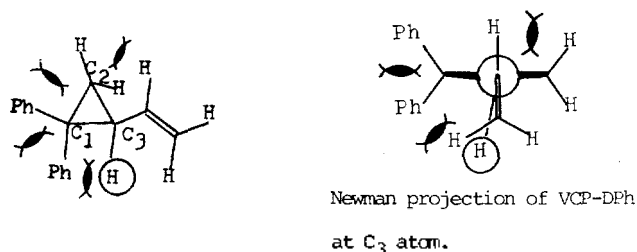
Singlet oxygen undergoes 1,4-cycloaddition with conjugated dienes to yield endoperoxides and the "ene" reaction with alkenes to give allylic hydroperoxides and 1,2-cycloaddition with electron-rich alkenes to form 1,2-dioxetanes. Depending on the nature of the substituents attached to the reaction centres and on the bulkiness of more distant parts of the molecule, stereoelectronic and steric effects determine the regioselectivity, the regioselectivity, the stereospecificity, and the stereoselectivity of the reactions and thus determine the product distributions observed with real systems.

Ene-product formation seems to be affected little by the nature of the solvent but is strongly dependent on the stereoelectronic and steric effects exerted by the olefin on the attacking electrophilic singlet oxygen. Substitution of olefinic hydrogens by electron-donating alkyl groups enhances the rate of ene-reactions with singlet oxygen. The reactivity of olefins toward singlet oxygen increases linearly with decreasing $\pi_{\text{C}=\text{C}}$ -ionization potentials of the olefins, *i.e.*, with higher occupied $\pi_{\text{C}=\text{C}}$ -orbitals.

The ene-mechanism requires that $^1\text{O}_2$ approaches the π system perpendicular to the double bond plane and, in addition, preferentially uses that allylic hydrogen which is oriented approximately orthogonal to the olefinic plane. Such

an orientation does not only provide for a closest approach between the allylic hydrogen and the oxygen atom which is not involved in C-O bonding, but also for a maximum overlap of the p -orbitals of the developing new π_{e-c} bond.

With regard to VCP-DPh, the conformation of 'axially positioned' allylic hydrogen atom is hindered by the two phenyl groups attached to C₁ atom of cyclopropane ring and the π -electron density of the vinyl group is not enough to produce photoene-product because of the absence of electron-donating groups attached to the vinyl group.



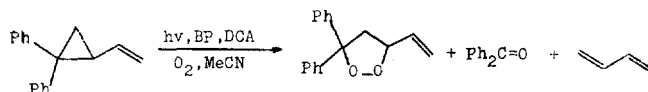
In most cases, 1,2-cycloaddition of singlet oxygen to olefins requires the presence of electron-donating groups in the alkene, such as -NR₂, -OR, and -SR. photooxygenation of alkyl-substituted olefins generally results in the formation of allylic hydroperoxides. However, if the ene reaction is precluded by the substitution pattern or for steric reasons, 1,2-dioxetanes or their cleavage products may be formed.

The enhanced reactivity of π -electron-rich olefins in 1,2-cycloaddition with singlet oxygen is in accord with the formulation of this species as an electrophilic reagent—a conclusion in harmony with its electronic structure. Bond formation thus requires transfer of electron density from the highest occupied molecular orbital (HOMO) of the olefin to the lowest unoccupied molecular orbital (LUMO) of singlet oxygen.

In the case of VCP-DPh, if the vinyl group is conjugated

with the two phenyl groups *via* π -character of the cyclopropane ring, the vinyl group is activated and undergoes 1,2-cycloaddition with singlet oxygen to yield 1,2-dioxetane. However, two phenyl groups attached to cyclopropane ring are not conjugated with the vinyl group and cyclopropane ring does not transmit the conjugation. Therefore, the vinyl group of VCP-DPh is not π -electron-rich and does not undergo 1,2-cycloaddition with singlet oxygen to produce 1,2-dioxetanes.

Cosensitized photooxygenation of VCP-DPh ($1 \times 10^{-2} M$) in oxygen-saturated acetonitrile solution with biphenyl ($1 \times 10^{-2} M$) and 9,10-dicyanoanthracene ($1 \times 10^{-4} M$) yielded 3,3-diphenyl-5-vinyl-1,2-dioxolane (64.8 % yield), benzophenone (35.2 % yield), and 1,3-butadiene.⁷



References

- (1) M. Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962).
- (2) J. Pete, *Bull. Soc. Chim. France*, **357** (1967).
- (3) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).
- (4) M. Charton in "The Chemistry of Alkenes," J. Zabicky Ed., Interscience Publishers, London, England, Vol. II, Chapter 10, 1970.
- (5) J. M. Stewart and G. K. Pagenkopf, *J. Org. Chem.*, **34**, 7 (1969).
- (6) S. C. Shim and S. W. Suh, *J. Korean Chem. Soc.*, **23**, 115 (1979).
- (7) The reaction was carried out at 10°C under oxygen with a Hanovia 450 W medium-pressure mercury arc lamp by using a CuSO₄-filter solution. 1,3-Butadiene was detected in brominated form, 1,2,3,4-tetrabromobutane.

Novel Dechlorination of Arylsulfonyl Chlorides with Superoxide Anion (O₂⁻)

Bong Chul Chung and Yong Hae Kim¹

*Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O. Box 150 Chongyangni
Seoul 131, Korea (Received October 6, 1984)*

The discovery of superoxide dismutase (SOD) by Fridovich and McCord in 1969¹ has considerably stimulated the investigation of superoxide anion radical (O₂⁻), not only in biochemistry but also in organic chemistry recently. Although commercially available potassium superoxide (KO₂), sodium superoxide (NaO₂), and ammonium superoxide (NH₄O₂), as sources of superoxide had been prepared, both its instability in protic solvents and its limited solubility in organic solvents such as dimethylsulfoxide (DMSO) and acetonitrile had prevented studies of the chemistry of superoxide ion. How-

ever, the observation of Valentine and Curtis in which KO₂ can be appreciably dissolved in aprotic solvents by complexation with crown ethers² has quickly promoted the use of this reagent for many reactions with simple organic substrates. Numerous reports dealing with reactions of various organic substrates with "naked" superoxide anion have appeared within only past five years. However, only a few sporadic works on the reaction of organic sulfur compounds with O₂⁻ appeared until oxidations of organic sulfur compounds with O₂⁻ in the presence of 18-crown-6-ether were initiated.³⁻⁶