

We propose a similar mechanism involving a cosensitizer radical cation and a sensitizer radical anion which subsequently reduces O₂ (Scheme I). The cosensitizer radical cation (BP^{•+}) then oxidizes the substrate VCP-DPh. The radical cation VCP-DPh^{•+} is generated in an open form that reacts with superoxide to form the biradicals A or B.⁹ These biradical intermediates close to give the cyclic peroxide 2 as the major product. However, if biradical A cleaves before it closes, it can give the carbonyl oxide that yields benzophenone and 1,3-butadiene. The latter was isolated as its tetrabromide.

The same photoproducts 2 and 3 were obtained by acetone-sensitized photooxygenation of 1, for which we propose the mechanism of Scheme II.

Direct irradiation of 1 at 253.7 nm in the absence of oxygen produces 1,1-diphenylethylene as the major product. A small amount of 4,4-diphenylcyclopentene was also formed, probably via the biradical intermediate from the initial cyclopropane ring opening.⁴

Experimental Section

Instruments. UV-vis absorption spectra were recorded on a Cary 17 spectrophotometer. ¹H and ¹³C NMR spectra were recorded with a Varian FT-80A spectrometer in chloroform-*d*. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer using the KBr pellets of a sodium chloride cell. Mass spectra were determined with a Hewlett Packard 5985A GC/MS system. Fluorescence spectra were recorded on an Aminco-Bowman spectrofluorometer with an Aminco XY recorder. Elemental analyses were carried out on a F&M Scientific Cooperation C-H-N Analyzer Model 180. HPLC analyses were performed with a μ -Porasil column eluted with *n*-hexane and ethyl acetate (17/1, v/v) at a flow rate of 1.5 mL/min on a Waters Associates Model 244 chromatography with UV detector.

Materials. 9,10-Dicyanoanthracene (Eastman) was recrystallized twice from pyridine. Biphenyl (Aldrich) was purified by vacuum sublimation. Rose Bengal (Aldrich) was used without further purification. Acetonitrile (UV grade, Burdick & Jackson Lab.) was successively refluxed over and distilled from phosphorus pentoxide and calcium hydride under nitrogen. Acetone (Merck), *n*-hexane (Merck), and other reagents were used as received. Kiesel-gel 60 GF₂₅₄ and Kiesel-gel 60 (Merck) were used for TLC and flash chromatography, respectively.

1,1-Diphenyl-2-vinylcyclopropane (VCP-DPh). 1,1-Diphenyl-2-vinylcyclopropane was prepared by thermal decomposition of diphenyldiazomethane in butadiene:¹⁰ ¹H NMR (CDCl₃) δ 7.33–6.97 (m, 10 H), 5.2–4.7 (m, 3 H), 2.20 (m, 1 H), 1.63–1.35 (m, 2 H); IR (NaCl cell) 3060 (s), 3020 (s), 2910 (sh), 2000–1700 (monosubstituted phenyl), 1635 (m), and 1015 cm⁻¹ (w); *n*_D²⁰ 1.5870; *d*₄²⁰ 1.019 g/cc.

Acetone-Sensitized Photooxygenation of VCP-DPh. VCP-DPh (0.22 g, 1 mmol) in 100 mL of acetone with irradiation ($\lambda > 290$ nm) under oxygen with a Hanovia 450-W medium-pressure mercury arc lamp. The reaction was monitored by HPLC and was completed in 12 h. The solvent was removed on a rotary evaporator, and the residue was subjected to column chromatography on silica gel (10 in. \times 1 in.) using successively 500 mL of ethyl acetate, 500 mL of acetone, and 300 mL of methanol. The ethyl acetate and acetone fractions were evaporated and subjected to preparative TLC to yield endoperoxide 2 as the major product and benzophenone (3) as a side product. Recrystallization of 2 from ethyl acetate yielded colorless needles: 3,3-diphenyl-5-vinyl-1,2-dioxolane (2), 226 mg (89.7%): ¹H NMR (CDCl₃) δ 7.65–7.30 (m, 10 H), 6.15–5.70 (m, 1 H), 5.50–5.20 (m, 2 H), 4.91 (q, *J* = 795 Hz, 1 H), 3.59 (dd, *J* = 12 and 7.5 Hz, 1 H), 3.16 (dd, *J* = 12 and 7.5 Hz, 1 H); ¹³C NMR (CDCl₃) 142.69, 142.40, 134.94, 128.25, 127.50, 126.46, 126.21, 19.08, 90.60, 82.80, 53.30; IR (KBr)

2000–1700 (monosubstituted phenyl), 1605 (m, vinyl C=C stretching), 1060 and 1035 cm⁻¹ (m, asymmetric C–O stretching); mass spectrum, *m/e* (rel intensity), 252 [M⁺] (0.9), 218 [M – H₂O⁺] (26.7), 142 [C₆H₅C₆H₅⁺] (24.1), 129 [C₆H₅C₄H₄⁺] (39.6), 105 [C₆H₅C₂H₄⁺] (55.9), 77 [C₆H₅⁺] (100); mp 92–92.5 °C. Anal. Calcd for C₁₇H₁₆O₂: C, 80.91; H, 6.30. Found: C, 80.92; H, 6.30.

Benzophenone (10 mg, 5.5%) was identified from its spectral properties and by comparison with an authentic sample. The evolved gases were trapped with 20 mL of Br₂/CHCl₃ (1/1, v/v) at –40 °C and the resulting reddish brown solution was stirred for 15 h at room temperature. After evaporation of excess bromine and solvent, the dark liquid crystallized on standing. The products were filtered, washed with cold ethanol, and recrystallized from ethanol to obtain colorless crystal (17.6 mg). The product was identified as 1,2,3,4-tetrabromobutane from its spectral properties and by comparison with an authentic sample. The gaseous product is thus proven to be 1,3-butadiene.

Cosensitized Photooxygenation of VCP-DPh with DCA and BP. Cosensitized photooxygenation was carried out in dry acetonitrile with 1 \times 10⁻² M VCP-DPh, 1 \times 10⁻² M BP, and 1 \times 10⁻⁴ M DCA. The solution was irradiated at 10 °C under oxygen sparging and through a CuSO₄ filter solution.¹¹ The reaction was completed in 8 h. The products were isolated by preparative silica gel TLC to obtain 64.8% of 3,3-diphenyl-5-vinyl-1,2-dioxolane (2) and 35.2% of benzophenone (3). 1,3-Butadiene was detected as described.

Registry No. 1, 57393-03-0; 2, 102261-93-8; 3, 119-61-9; 4, 106-99-0; DCA, 1217-45-4; BP, 92-52-4; diphenyldiazomethane, 883-40-9; acetone, 67-64-1; 1,2,3,4-tetrabromobutane, 1529-68-6.

(11) The 1-cm pathlength filter solution was prepared from 27 g of CuSO₄·H₂O, 30 g of NaNO₂, and 50 mL of concentrated NH₄OH diluted with water to 1000 mL.

Organic Sonochemistry. New Ultrasonically Accelerated Reactions Involving Lithium

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There is a growing list of successful applications of ultrasonic waves to organic syntheses.¹ To this we wish to add the significant rate enhancements that ultrasound produces when the substrates given in Table I are treated with lithium.^{1a,b} All reactions were run at room temperature with 20–50% excess lithium dispersion or powder. In the absence of ultrasonic waves the reaction times were 2–5 times longer.

The reaction of α,α' -dibromo-*o*-xylene with lithium is noteworthy (Scheme I) because it does not lead to *o*-xylylene, the major product obtained when zinc is used.² Evidence against *o*-xylylene formation and in favor of an ionic intermediate is the isolation of α,α' -bis(trimethylsilyl)-*o*-xylene when trimethylchlorosilane is present as a trap.

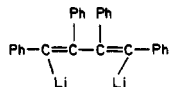
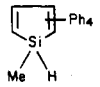
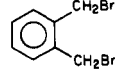
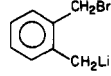
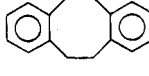
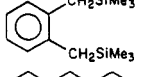
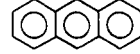
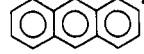
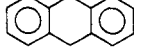



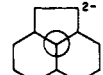
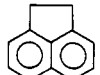
(1) (a) For other reactions involving lithium and ultrasound, see: Boudjouk, P.; and Han, B.-H. *Tetrahedron Lett.* 1981, 22, 3814. Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* 1982, 104, 4992. Azuma, T.; Yanagida, S.; Sakurai, H.; Sasa, S.; Yoshino, K. *Synth. Commun.* 1982, 12, 137. Masamune, S.; Murakami, S.; Lobita, H. *Organometallics* 1983, 2, 1464. (b) Ultrasound promotes lithium-halide exchange: Luche, J. L.; Damiano, J. C. *J. Am. Chem. Soc.* 1980, 102, 7926. Boudjouk, P.; Han, B.-H. *Tetrahedron Lett.* 1981, 22, 2757. (c) For recent reviews of ultrasonically accelerated reactions, see: Boudjouk, P. *NCHR. Chem., Tech. Lab.* 1983, 31, 798. Boudjouk, P. *J. Chem. Educ.*, in press. (2) Han, B.-H.; Boudjouk, P. *J. Org. Chem.* 1982, 47, 751.

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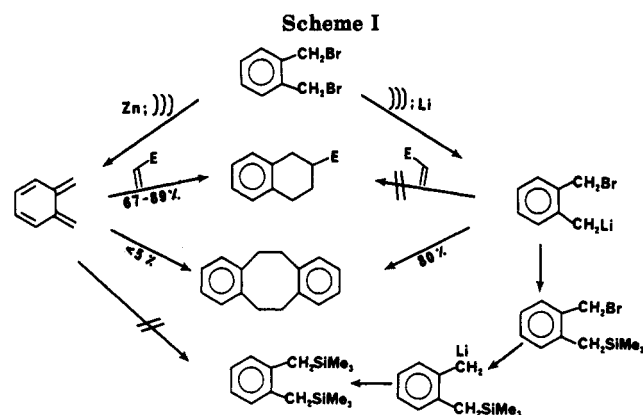
(9) Alternatively, ground-state oxygen could add to VCP-DPh^{•+} with subsequent reduction of the peroxy radical cation by O₂⁻, DCA^{•-}, VCP-DPh, or BP.

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Table I. Ultrasonically Accelerated Lithiation Reactions

substrate	organolithium	time, min	electrophile	product	yield, (%)
PhC≡CPh		10	MeHSiCl ₂		68 ^a
PhC≡CH	PhC≡CLi	5	MeI	PhC≡CMe	95 ^a
		60-90			80
		60-90	Me ₃ SiCl		45 ^b
		30-45	H ₂ O		90
		10	Me ₃ SiCl	c-C ₈ H ₈ (SiMe ₃) ₂	82 ^c
		60-90	MeOH		90 ^d

^a Electrophiles were added to anion solution at -78 °C. ^b The reaction was carried out in the presence of (CH₃)₃SiCl. ^c NMR of the anion⁴ indicates quantitative conversion. After Me₃SiCl is added, the product is a mixture of several isomers.⁵ ^d Traces of 1,5-dihydroacenaphthylene were present.⁶



When Zn is the reducing metal, no silyl derivative was isolated.² Moreover, zinc-reduced α,α' -dibromo-*o*-xylene readily undergoes cycloaddition reactions with dienophiles and polymerizes in the absence of a trap.² With lithium, however, the dibromide gives no measurable quantities of cycloaddition products with maleic anhydride and other dienophiles but gives very good yields of the dimer 5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene in the absence of a quenching agent. We believe the intermediate responsible for the formation of the dimer and the bis silyl derivative is the monoanion drawn in Scheme I. Although we have not been able to rule out α,α' -dilithio-*o*-xylene as a possibility, it seems very unlikely that it is playing an important role in these reactions, especially in the formation of the dimer.

Experimental Section

Tetrahydrofuran (THF) was distilled from benzophenone ketyl just prior to use. Lithium was used as a dispersion (30%) or as powder. When lithium dispersion was used, the mineral oil was removed by washing with THF. A Branson Model 220 ultrasonic laboratory cleaner (117 V, 150 W, 50/60 Hz) was used for these experiments. All products were characterized by comparison of their properties with those of authentic samples.

Preparation of 1-Methyl-2,3,4,5-tetraphenylsilole. Lithium dispersion (0.45 g, 19 mmol, 30% in mineral oil) was placed in a dry nitrogen-filled 25-mL three-neck flask and washed (2 × 20 mL) with tetrahydrofuran (THF). To this was added 12 mL of THF and 3.0 g (16.8 mmol) of diphenylacetylene followed by

sonication in the ultrasonic laboratory cleaner. The reaction mixture turned dark blue instantly. After 10 min the flask was removed from the sonicator, cooled to -78 °C, and treated with 6.6 g (57 mmol) of methyldichlorosilane in 6 mL of THF. Volatiles were pumped off after the reaction was stirred for 30 min at room temperature. The analytically pure product 1-methyl-2,3,4,5-tetraphenylsilole³ was isolated (2.13 g, 68%) by column chromatography (neutral alumina; 1:1 benzene-chloroform) followed by crystallization (acetone).

Reactions 2 and 4-6 (Table I) were carried out with analogous procedures. In reaction 5, the NMR of the anion indicates quantitative conversion.⁴ After adding Me₃SiCl, the product is a mixture of several isomers.⁵ In reaction 6, in addition to acenaphthene, traces of 1,5-dihydroacenaphthylene were present.⁶

The Reaction of α,α' -Dibromo-*o*-xylene with Lithium. α,α' -Dibromo-*o*-xylene (2 g, 7.6 mmol) in 10 mL of THF was added to a suspension of 0.12 g (17 mmol) of Li powder in 5 mL of THF in a three-neck round-bottom flask under N₂. The contents were sonicated for 60 min. Afterwards, solvent was evaporated under reduced pressure, and the residue was chromatographed on a 2.5 × 10 cm column of neutral alumina by using methylene chloride as eluent. After the solvent was removed the dibenzocyclooctene (0.64 g, 80%) was obtained as white needles, mp 106-107 °C (lit.⁷ mp 109-110 °C).

A similar experiment was carried out in the presence of 1.8 g (16 mmol) of trimethylchlorosilane and 0.24 g (634 mmol) of lithium; after workup, an analytical sample of 1,2-bis[(trimethylsilyl)methyl]benzene⁸ was obtained by preparative GC. The yield was estimated by GC to be 45%.

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Registry No. PhC≡CPh, 501-65-5; MeHSiCl₂, 75-54-7; PhC≡CH, 536-74-3; MeI, 74-88-4; PhC≡CMe, 673-32-5; Me₃SiCl, 75-77-4; c-C₈H₈(SiMe₃)₂, 102438-21-1; 1-methyl-2,3,4,5-tetraphenylsilole, 4071-99-2; cyclooctatetraene, 629-20-9; α,α' -dibromo-*o*-xylene, 91-13-4; 5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene, 1460-59-9; anthracene, 120-12-7; 9,10-dihydroanthracene, 613-31-0; acenaphthylene, 208-96-8; 1,2-dihydroacenaphthylene, 83-32-9; 1,2-bis[(trimethylsilyl)methyl]benzene, 17557-09-4.

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