

*Anal.* Calcd for  $C_{17}H_{10}O$ : C, 87.35; H, 4.98. Found: C, 87.47; H, 5.00.

**4-Vinylphenanthrene.**—A mixture of 175 mg of methyltriphenylphosphonium bromide, 0.25 ml of 1.91 *M* phenyllithium, and 20 ml of dry ether were stirred and refluxed under nitrogen for 0.5 hr. A solution of 100 mg of 4-phenanthrenecarboxaldehyde in 20 ml of ether was added dropwise over a period of 15 min, and the mixture was then stirred and refluxed for 2 hr. The reaction mixture was filtered, the filtrate diluted with 200 ml of ether, washed with water, dried, and filtered, and the ether removed *in vacuo*. The residue was chromatographed on alumina using hexane as the eluent to give an oil which was further purified and analyzed *via* the picrate: 125 mg (59.1% yield), mp 112–113°.

*Anal.* Calcd for  $C_{22}H_{15}N_3O_7$ : C, 60.97; H, 3.49; N, 9.70. Found: C, 60.85; H, 3.49; N, 9.53.

**Photocyclization of 2-Vinylbiphenyl.**—A  $10^{-3}$  *M* solution of **8** in benzene was placed in a Pyrex test tube and irradiated under aerobic conditions for 1 hr. Gas chromatographic analysis of the reaction mixture showed it to consist entirely of **10**. In a second experiment a solution of 2.0 g of **8** in 1 l. of benzene was stirred and irradiated through a Vycor immersion well. The course of the reaction was followed using pmr and uv spectroscopy. The reaction was stopped after 12 hr, at which point it was ~70% complete. Judging by the color of the solution, considerable photodecomposition had occurred. The solvent was removed *in vacuo* and the residual liquid vacuum distilled to give 400 mg [bp 181–183° (4.5 Torr)] of material. A pmr spectrum of this mixture showed it to consist of **8** and **10**. No further attempts were made to isolate the low melting **10**.

**Photocyclization of 4-Vinylphenanthrene.**—A  $10^{-2}$  *M* solution of **12** in benzene was placed in a Pyrex test tube and irradiated under aerobic conditions for 1 hr. The reaction mixture was analyzed by gas chromatography and contained  $26 \pm 2\%$  **15** and  $74 \pm 2\%$  **14**. There was no detectable amount of starting material or other compounds present. Irradiation of solutions of **12** under anaerobic conditions, followed by gas chromatographic analysis, showed the presence of **14**; there was no evidence of pyrene.

**Isolation of 4,5-Dihydropyrene.**—Four 20-ml benzene solutions, each  $2 \times 10^{-3}$  *M* in **12**, were placed in Pyrex test tubes, degassed, and irradiated for 0.5 hr. The solutions were combined, the solvent was removed *in vacuo*, and the residue was sublimed. 4,5-Dihydropyrene, **14**, sublimed at 75° (2.0 Torr): mp 132–134° (lit.<sup>13</sup> 131–132°); pmr  $\delta$  3.29 (s, 4 H), 7.55 (m, 8 H).

**Registry No.**—**8**, 1587-22-0; **12**, 41498-39-9; **12** picrate, 41498-40-2; **14**, 6628-98-4; 4-methylphenanthrene, 832-64-4; 4-phenanthrenecarboxaldehyde, 41498-43-5.

(13) M. S. Newman and H. W. Whitehouse, *J. Amer. Chem. Soc.*, **71**, 3664 (1949).

## Photosensitized Cyclodimerization of Phenyl Vinyl Ethers

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Recently we have reported that aromatic esters, substituted with electron-withdrawing groups, undergo photocycloadditions to olefins to yield oxetanes<sup>1a,b</sup> or ladder compounds,<sup>1c</sup> and that these esters are readily photoreduced by various aromatic hydrocarbons.<sup>2</sup> In

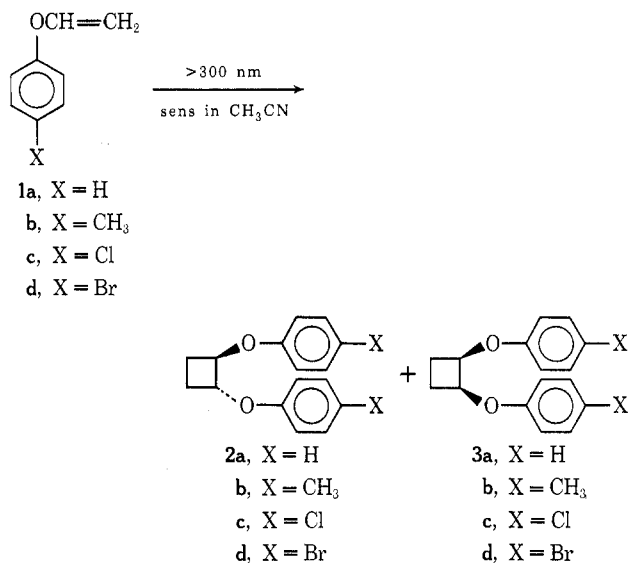
(1) (a) Y. Shigemitsu, H. Nakai, and Y. Odaira, *Tetrahedron*, **25**, 3039 (1969); (b) Y. Shigemitsu, Y. Katsuhara, and Y. Odaira, *Tetrahedron Lett.*, 2887 (1971); (c) Y. Katsuhara, T. Nakamura, A. Shimizu, Y. Shigemitsu, and Y. Odaira, *Chem. Lett.*, 1215 (1972).

(2) (a) K. Fukui and Y. Odaira, *Tetrahedron Lett.*, 5255 (1969); (b) K. Fukui, K. Senda, Y. Shigemitsu, and Y. Odaira, *J. Org. Chem.*, **37**, 3176 (1972).

the course of a continuing study we also found that aromatic esters acted as sensitizers for cyclodimerization of phenyl vinyl ether **1a** to give its head-to-head cyclodimers **2a** and **3a**.<sup>3</sup> For some olefins having an electron-withdrawing group, such as acrylonitrile, photosensitized cyclodimerization is well known,<sup>4</sup> but, for olefins having an electron-donating group, such a reaction is very unique.

In this paper, we wish to report that in the presence of aromatic esters some para-substituted phenyl vinyl ethers **1b–d** also undergo photosensitized cyclodimerizations to afford head-to-head cyclodimers. Furthermore, we examined the availability of various sensitizers to effect this reaction and the quenching efficiency of a sensitizer's (dimethyl terephthalate, **4**) fluorescence by the ethers **1a–e** in order to clarify the reaction mechanism.

Irradiation of an acetonitrile solution of **1** and a sensitizer such as dimethyl terephthalate (**4**) gave a mixture of *trans*- and *cis*-1,2-di-*para*-substituted phenoxycyclobutanes **2** and **3** (3:4) as the result of head-to-



head cyclodimerization of **1**. The structures of the cyclodimers were determined by their mass and nmr spectra. From mass spectra, they were characterized to be the head-to-head cyclodimers due to the reverse [2 + 2] cleavage ( $M^+ - C_2H_4$ ). The stereochemistry of **2** and **3** was confirmed by comparison of their nmr spectra with those of *trans*- and *cis*-1,2-dibromocyclobutanes. A methine proton chemical shift of **2** was more upfield by *ca.* 0.2 ppm than that of **3**. In addition, the former had a broad four-proton methylene peak, while the latter had a sharp and sometimes distinct triplet methylene peak. These features of nmr spectra are very similar to those of *trans*- and *cis*-1,2-dibromocyclobutanes whose stereochemistry is confirmed.<sup>5</sup> On the basis of these nmr data, **2** and **3** were assigned to the *trans* and *cis* isomers, respectively.

On the other hand, irradiation of **1** without the sensitizer gave no cyclodimer but only polymers.<sup>6</sup> This indicates that the cyclodimerization of **1** proceeds ex-

(3) S. Kuwata, Y. Shigemitsu, and Y. Odaira, *J. Chem. Soc., Chem. Commun.*, 2 (1972).

(4) S. Hosaka and S. Wakamatsu, *Tetrahedron Lett.*, 219 (1968).

(5) P. I. Abell and C. Chiao, *J. Amer. Chem. Soc.*, **82**, 3610 (1960).

(6) Cyclodimers **2** and **3** remained unchanged upon similar irradiation.

clusively through photosensitization. To ascertain the dependence of the nature of sensitizer on this cyclodimerization, **1a** was irradiated in the presence of various sensitizers. The results are summarized in Table I.

TABLE I  
RESULTS OF PHOTOSENSITIZED REACTIONS OF **1a**  
WITH SOME SENSITIZERS

Sensitizer	$E_T$ , kcal/mol	Nature of lowest triplet state	2a and 3a
Methyl benzoate	77.9	$\pi-\pi^*$	Yes
Dimethyl terephthalate <sup>a</sup>	73.1	$\pi-\pi^*$	Yes
Benzonitrile	77	$\pi-\pi^*$	Yes
Benzene <sup>b</sup>	85	$\pi-\pi^*$	No
Anisole	80.7	$\pi-\pi^*$	No
Acetophenone <sup>a</sup>	73.6	$n-\pi^*$	No
Benzophenone <sup>a</sup>	69.5	$n-\pi^*$	No

<sup>a</sup> Irradiated through Pyrex. Others were irradiated through quartz. <sup>b</sup> Irradiated in the benzene solution.

As shown in Table I, effective sensitizers for the cyclodimerization are aromatic esters and benzonitrile, which have  $\pi-\pi^*$  type lowest excited states and have an electron-withdrawing group in their benzene ring. Furthermore, the possibility of exothermic triplet-triplet energy transfer from these sensitizers to **1a** should be eliminated, because the  $E_T$  of **1a** is estimated at 80.2 kcal/mol from the 0-0 band of phosphorescence (MeOH-EtOH glass), which is above that of the sensitizer. On the other hand, acetophenone and benzophenone having  $n-\pi^*$  type lowest excited states do not sensitize this cyclodimerization but only undergo well-known Paterno-Büchi reaction to yield oxetane derivatives.<sup>7</sup> This dramatic dependency of cyclodimerization on the nature of the sensitizer could be of much help for determining reaction mechanism.

Uv spectra showed no evidence for a charge-transfer complex of the sensitizer with the ether. Although these results suggest the participation of an excited singlet state of the sensitizer, it is still in question how this state acts in the primary step of the photosensitized reaction. Thus we conducted a quenching experiment of the fluorescence of a sensitizer **4** by **1**. The Stern-Volmer plots showed comparatively good linearity, and  $k_q\tau$  values are given in Table II. From this table, we

TABLE II  
 $k_q\tau$  VALUES OF PHENYL VINYL ETHERS FOR FLUORESCENCE  
QUENCHING OF DIMETHYL TEREPHTHALATE (**4**) IN ACETONITRILE

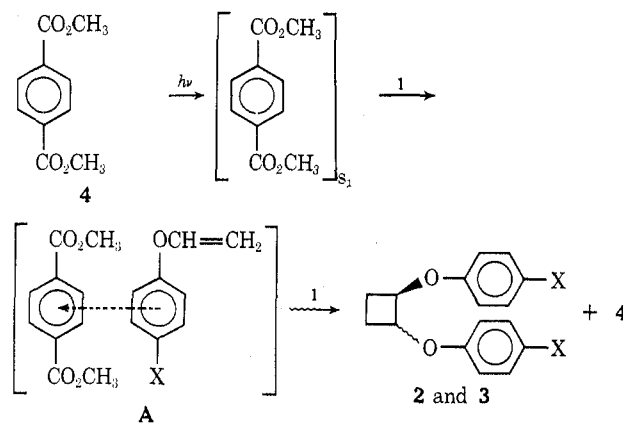
Quencher	$k_q\tau \times 10^{-1}, M^{-1}$
<b>1a</b>	3.6
<b>1b</b>	4.6
<b>1c</b>	3.7
<b>1d</b>	4.0
<i>m</i> -Chlorophenyl vinyl ether ( <b>1e</b> )	3.6
Anisole	5.1
Phenetole	4.5

can find (1) that the  $k_q\tau$  value of phenetole, having no vinyl group, is very close to those of **1**; (2) that the  $k_q\tau$  value of **1** follows the order of increasing electron density on the benzene ring of **1**. From these facts we

(7) S. Kuwata, unpublished results.

conclude that the primary step toward product formation may be exciplex formation between an excited singlet sensitizer and a ground-state ether **1** (A), and that the interaction may localize between both benzene rings where the one of the sensitizer may act as the acceptor and that of the second as the donor.

At the present time we would like to propose the following reaction scheme for cyclodimerization of **1**.



Further studies on the detailed mechanism for this reaction are in progress and will be published shortly.

#### Experimental Section

All melting points are uncorrected. Ir spectra were obtained on a Japan Spectroscopic Model IR-G spectrophotometer in a potassium bromide pellet. Nmr spectra were obtained with a Nippon Denshi Model JNM-3H 60 spectrometer in carbon tetrachloride using tetramethylsilane as an internal standard. Mass spectra were obtained with a Hitachi Model RMU-6E mass spectrometer. Uv spectra were obtained with a Hitachi 124 spectrophotometer in acetonitrile solution. Fluorescence spectra were obtained with a Hitachi fluorescence spectrophotometer MPF-3 in acetonitrile solution.

**Materials.**—Phenyl vinyl ethers were prepared by the method of McElvain<sup>8</sup> from ethylene dibromide and appropriate substituted or nonsubstituted phenols. Appropriate  $\beta$ -bromophenoles were given by refluxing a mixture of ethylene dibromide, sodium hydroxide, and phenols in water. They were purified by distillation and dehydrobrominated to appropriate phenyl vinyl ethers by heating at *ca.* 200° with a nearly equal amount (in weight) of powdered potassium hydroxide in a copper flask. The phenyl vinyl ethers were purified by distillation: **1a**, bp 154° (760 mm),  $n_D^{25}$  1.5212, uv max 269 nm ( $\epsilon$   $1.0 \times 10^3$ ); **1b**, bp 71–76° (18 mm),  $n_D^{25}$  1.5170, uv max 274 nm ( $\epsilon$   $1.09 \times 10^3$ ); **1c**, bp 70–72° (13 mm),  $n_D^{25}$  1.5408, uv max 278 nm ( $\epsilon$   $1.23 \times 10^3$ ); **1d**, bp 101.5–104° (24 mm),  $n_D^{25}$  1.5658, uv max 279 nm ( $\epsilon$   $1.18 \times 10^3$ ); **1e**, bp 89.5–93.5° (26–26.5 mm),  $n_D^{25}$  1.5354, uv max 273 nm ( $\epsilon$   $1.29 \times 10^3$ ), 280 ( $1.15 \times 10^3$ ). The sensitizers were purified by distillation or recrystallization before use.

**Reaction of Phenyl Vinyl Ether (1a).**—A solution of **1a** (6.0 g, 0.05 mol) and **4** (4.0 g, 0.021 mol) in 150 ml of acetonitrile was irradiated for 15 hr with a 500-W high-pressure mercury arc through Pyrex under nitrogen at room temperature. After evaporation of the solvent *in vacuo*, the resulting precipitate of **4** (3.5 g) was removed by filtration and washed with a few portions of cooled ether. The filtrate combined with the ether portions was concentrated and distilled under reduced pressure, recovering unreacted **1a** (2.9 g). The resulting brown-colored oily residue was chromatographed on a silica gel. The cyclodimers **2a** and **3a** (0.92 g, **2a**:**3a** *ca.* 3:4, 30%) were eluted with benzene-petroleum ether (bp 30–60°) (1:49) and recrystallized from petroleum ether. **2a** had mp 66–68°; ir 1595, 1585, 1490, 1480, 1240, 1220, 1065, 920, 745, 685  $\text{cm}^{-1}$ ; nmr  $\tau$  2.6–3.3 (m, 10 H), 5.2–5.5 (m, 2 H),

(8) S. M. McElvain and B. Fajardo-Pinzón, *J. Amer. Chem. Soc.*, **67**, 650 (1945).

7.4–8.0 (broad m, 2 H), 8.0–8.75 (broad m, 2 H); mass spectrum  $m/e$  240 ( $M^+$ ), 212 ( $M^+ - C_2H_4$ ), 120 ( $M^+/2$ ).

Anal. Calcd for  $C_{16}H_{16}O_2$ : C, 79.97; H, 6.71. Found: C, 80.11; H, 6.80.

**3a** had mp 80.0–80.5°; ir 1600, 1585, 1490, 1235, 1210, 1090, 915, 750, 690  $cm^{-1}$ ; nmr  $\tau$  2.7–3.4 (m, 10 H), 5.1–5.35 (m, 2 H), 7.65–7.85 (d, with shoulder, 4 H); mass spectrum  $m/e$  240 ( $M^+$ ), 212 ( $M^+ - C_2H_4$ ), 120 ( $M^+/2$ ).

Anal. Calcd for  $C_{16}H_{16}O_2$ : C, 79.97; H, 6.71. Found: C, 79.91; H, 6.91.

Similar experimental procedures were used for the photosensitized cyclodimerizations of **1b–d** with **4** unless otherwise stated. Trans and cis cyclodimers were always obtained in ca. 3:4 ratio and recrystallized from petroleum ether.

**Cyclodimers 2b and 3b.**—Cyclodimers **2b** and **3b** were obtained in 15% yield. **2b** had mp 64–65°; ir 1610, 1580, 1500, 1240, 1220, 1055, 915, 810  $cm^{-1}$ ; nmr  $\tau$  2.9–3.4 (double d, 8 H), 5.25–5.65 (m, 2 H), 7.45–8.05 (broad m, 2 H), 8.05–8.6 (broad m, 2 H), 7.75 (s, 6 H); mass spectrum  $m/e$  268 ( $M^+$ ), 240 ( $M^+ - C_2H_4$ ), 134 ( $M^+/2$ ).

Anal. Calcd for  $C_{18}H_{20}O_2$ : C, 80.56; H, 7.51. Found: C, 80.61; H, 7.56.

**3b** had mp 47–47.5°; ir 1610, 1580, 1500, 1220, 1100, 905, 805  $cm^{-1}$ ; nmr  $\tau$  2.95–3.55 (double d, 8 H), 5.1–5.4 (m, 2 H), 7.65–7.9 (hindered by  $CH_3$  proton peak, 4 H), 7.75 (s, 6 H); mass spectrum  $m/e$  268 ( $M^+$ ), 240 ( $M^+ - C_2H_4$ ), 134 ( $M^+/2$ ).

Anal. Calcd for  $C_{18}H_{20}O_2$ : C, 80.56; H, 7.51. Found: C, 80.52; H, 7.38.

**Cyclodimers 2c and 3c.**—Similar irradiation of **1c** with tetramethyl pyromellitate as a sensitizer afforded cyclodimers **2c** and **3c** in 17% yield. **2c** had mp 89–90.5°; ir 1590, 1580, 1485, 1240, 1220, 1050, 920, 820  $cm^{-1}$ ; nmr  $\tau$  2.75–3.05 (d, 4 H), 3.10–3.40 (d, 4 H), 5.30–5.65 (m, 2 H), 7.40–7.95 (broad m, 2 H), 7.95–8.60 (broad m, 2 H); mass spectrum  $m/e$  308 ( $M^+$ ), 280 ( $M^+ - C_2H_4$ ), 154 ( $M^+/2$ ).

Anal. Calcd for  $C_{16}H_{14}Cl_2O_2$ : C, 62.15; H, 4.56. Found: C, 62.14; H, 4.46.

**3c** had mp 76–77°; ir 1590, 1485, 1230, 1080, 920, 820, 805  $cm^{-1}$ ; nmr  $\tau$  2.75–3.10 (d, 4 H), 3.20–3.55 (d, 4 H), 5.10–5.40 (m, 2 H), 7.65–7.85 (t, 4 H); mass spectrum  $m/e$  308 ( $M^+$ ), 280 ( $M^+ - C_2H_4$ ), 154 ( $M^+/2$ ).

Anal. Calcd for  $C_{16}H_{14}Cl_2O_2$ : C, 62.15; H, 4.56. Found: C, 62.32; H, 4.50.

**Cyclodimers 2d and 3d.**—Cyclodimers **2d** and **3d** were obtained in 7% yield. **2d** had mp 81–81.5°; ir 1585, 1480, 1230, 1050, 915, 815  $cm^{-1}$ ; nmr  $\tau$  2.6–2.9 (d, 4 H), 3.15–3.45 (d, 4 H), 5.2–5.6 (m, 2 H), 7.4–8.0 (broad m, 2 H), 8.0–8.5 (broad m, 2 H); mass spectrum  $m/e$  400 ( $M^+ + 4$ ), 398 ( $M^+ + 2$ ), 396 ( $M^+$ ), 368 ( $M^+ - C_2H_4$ ), 198 ( $M^+/2$ ).

Anal. Calcd for  $C_{16}H_{14}Br_2O_2$ : C, 48.24; H, 3.52. Found: C, 48.12; H, 3.47.

**3d** had mp 102.5–103.5°; ir 1580, 1480, 1225, 1065, 920, 820, 805  $cm^{-1}$ ; nmr  $\tau$  2.65–2.95 (d, 4 H), 3.25–3.55 (d, 4 H), 5.1–5.4 (m, 2 H), 7.65–7.80 (t, 4 H); mass spectrum  $m/e$  400 ( $M^+ + 4$ ), 398 ( $M^+ + 2$ ), 396 ( $M^+$ ), 368 ( $M^+ - C_2H_4$ ), 198 ( $M^+/2$ ).

Anal. Calcd for  $C_{16}H_{14}Br_2O_2$ : C, 48.24; H, 3.52. Found: C, 48.43; H, 3.57.

**Photolysis of 1a.**—An acetonitrile solution (45 ml) of **1a** (2.4 g, 0.02 mol) was irradiated for 98 hr with a 500-W high-pressure mercury arc through quartz under nitrogen at room temperature. After removal of the solvent *in vacuo*, unreacted **1a** (1.1 g) was recovered by distillation under reduced pressure. The resulting oily residue was chromatographed on 25 g of silica gel; cyclodimers **2a** and **3a** were not obtained but only polymers.

**Reaction of 1a with Various Sensitizers.**—An acetonitrile solution of **1a** was irradiated with a 500-W high-pressure mercury arc under nitrogen in the presence of benzonitrile, benzene (neat), anisole, acetophenone, or benzophenone under the conditions that a sensitizer predominantly absorbed the light. The cyclodimers **2a** and **3a** were identified by means of glc. The results are summarized in Table I.

**Quenching of Fluorescence of 4.**—The broad fluorescence of **4** in acetonitrile (0.085 *M*) was observed at 380 nm, which was quenched by the addition of **1** ( $2.5 \sim 13 \times 10^{-3}$  *M*). The intensity of emission (*F*) was compared to the intensity (*F*<sub>0</sub>) in the absence of **1**. Typical Stern–Volmer quenching plots (*F*<sub>0</sub>/*F* vs. molarity of **1**) were obtained. The slopes of plots give values for  $k_q\tau$ , where  $k_q$  is a rate constant for fluorescence quenching of **4** by **1** and  $\tau$  is the lifetime of fluorescence in the absence of **1**. The results are given in Table II.

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**Registry No.**—**1a**, 766-94-9; **1b**, 1005-62-5; **1c**, 1074-56-2; **1d**, 1005-61-4; **1e**, 1005-41-0; **2a**, 35370-70-8; **2b**, 41507-17-9; **2c**, 41507-18-0; **2d**, 41507-19-1; **3a**, 35370-71-9; **3b**, 41507-21-5; **3c**, 41507-22-6; **3d**, 41507-23-7; **4**, 120-61-6.

### On the Photodecarbonylation of $\beta,\gamma$ -Epoxy Ketones

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In contrast to the extensive investigation of the photochemistry of  $\alpha,\beta$ -epoxy ketones,<sup>1</sup>  $\beta,\gamma$ -epoxy ketones have received relatively little attention. Padwa and his coworkers have reported that irradiation of *trans*-1,4-diphenyl-3,4-epoxybutan-1-one affords products derived from Norrish type II processes, but the *cis* isomer gives only recovered starting material.<sup>2</sup> In 10-oxatricyclo[4.3.1.0<sup>1,6</sup>]decan-8-one, Norrish type II processes are not possible, and photolysis of this compound provides small amounts (less than 0.2 mol/mol of ketone) of a mixture of carbon monoxide and carbon dioxide, and a mixture of unidentified products.<sup>3</sup> Analogous to their cyclopropyl counterparts,<sup>4</sup> 2-(oxiranyl)cycloalkanones give (among other products) unsaturated macrolides by a three-atom photochemical ring expansion.<sup>5</sup>

Recently, Chambers and Marples have noted the photodecarbonylation of a  $\beta,\gamma$ -epoxy ketone.<sup>6</sup> Irradiation of 9 $\alpha$ ,10 $\alpha$ -epoxy ketone **1** results in the formation of unsaturated epoxide **2** (20%), the B-nor epoxide **3** (3%), and several minor products.<sup>6</sup> We now wish to report the photochemistry of two  $\beta,\gamma$ -epoxy ketones which also undergo photodecarbonylation to provide unsaturated epoxides. However, these reactions proceed in high chemical yield and by a mechanism clearly different from that reported by Chambers and Marples for the photodecarbonylation of **1**.

Treatment of hexamethylbenzobicyclo[2.2.2]octadienone **4'** with *m*-chloroperbenzoic acid gives epoxy

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(5) R. G. Carlson, J. H.-A. Huber, and D. E. Henton, *Chem. Commun.*, 223 (1973).

(6) R. J. Chambers and B. A. Marples, *Chem. Commun.*, 1122 (1972).

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