

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 τ 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 τ 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 τ 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 τ 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 τ 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 τ 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 τ 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*₀) in the absence of **1**. Typical Stern–Volmer quenching plots (*F*₀/*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 τ 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 β,γ -Epoxy Ketones

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In contrast to the extensive investigation of the photochemistry of α,β -epoxy ketones,¹ β,γ -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.² In 10-oxatricyclo[4.3.1.0^{1,6}]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.³ Analogous to their cyclopropyl counterparts,⁴ 2-(oxiranyl)cycloalkanones give (among other products) unsaturated macrolides by a three-atom photochemical ring expansion.⁵

Recently, Chambers and Marples have noted the photodecarbonylation of a β,γ -epoxy ketone.⁶ Irradiation of 9 α ,10 α -epoxy ketone **1** results in the formation of unsaturated epoxide **2** (20%), the B-nor epoxide **3** (3%), and several minor products.⁶ We now wish to report the photochemistry of two β,γ -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

(1) For reviews see A. Padwa, *Org. Photochem.*, **1**, 91 (1967); R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966, pp 129–140; J. A. Waters, Y. Kondo, and B. Witkop, *J. Pharm. Sci.*, **61**, 321 (1972).

(2) A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *J. Amer. Chem. Soc.*, **89**, 4435 (1967).

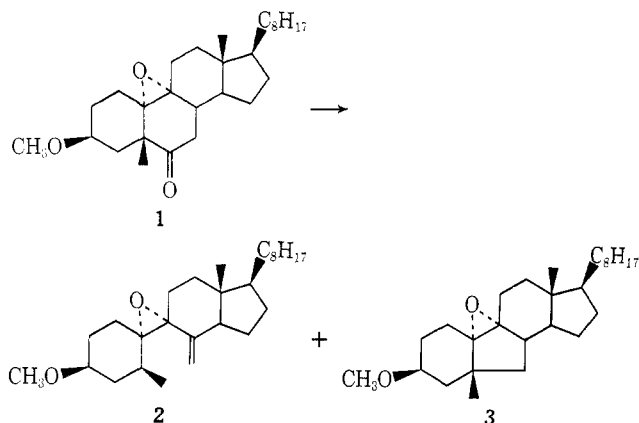
(3) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

(4) R. G. Carlson and E. L. Biersmith, *Chem. Commun.*, 1049 (1969).

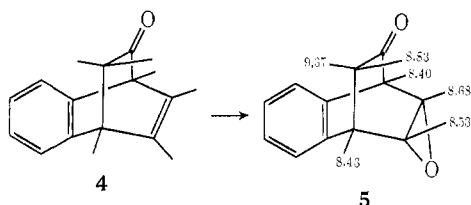
(5) R. G. Carlson, J. H.-A. Huber, and D. E. Henton, *Chem. Commun.*, 223 (1973).

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

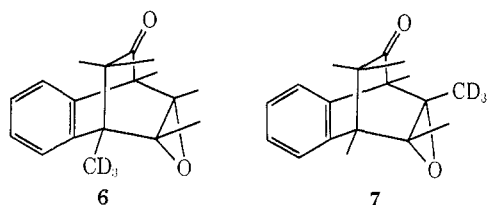
(7) A. C. Gripper-Gray and H. Hart, *J. Amer. Chem. Soc.*, **90**, 2569 (1968).



ketone **5**: mp 83–85°; $\nu_{\text{C=O}}^{\text{CDCl}_3}$ 1720 cm^{-1} ; pmr (CDCl_3) three-proton singlets at τ 9.37, 8.83, 8.68, 8.53, 8.43, and

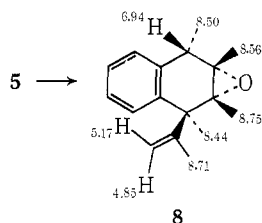


8.40, and a four-proton aromatic multiplet, τ 2.92–2.60. As the signals at τ 8.43 and 8.68 are absent in the pmr spectra of **6** and **7**, respectively, the pmr signals of **5**



can be assigned as indicated in the figure. The chemical shifts, and the difference in chemical shifts, of the methyls at C-7 and C-8 in **5** preclude the epoxy group in **5** from being anti to the benzene ring.

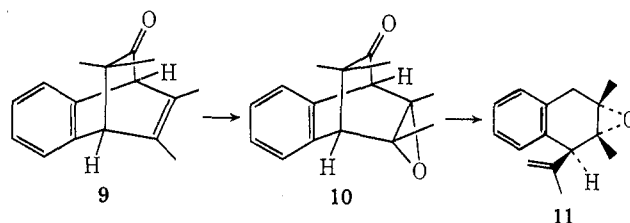
Irradiation of an ether solution of **5** through a Corex filter with a Hanovia L 450-W lamp affords unsaturated



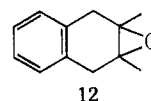
epoxide **8** in ca. 95% yield. The photoproduct (parent peak at m/e 242) is an oil which lacks carbonyl absorption in the infrared region and has an ultraviolet maximum (C_6H_{12}) at 285 nm (ϵ 149). The pmr (CDCl_3) spectrum of **8** consists of three-proton singlets at τ 8.75, 8.71, 8.56, and 8.44, a three-proton doublet ($J = 7$ Hz) at τ 8.50, a one-proton quartet ($J = 7$ Hz) at τ 6.94, a one-proton multiplet at τ 5.17, a broad one-proton singlet at τ 4.85, and a four-proton aromatic multiplet centered at τ 2.94. In the pmr spectra of the corresponding unsaturated epoxides obtained from the photodecarbonylations of **6** and **7**, the three-proton singlets are absent at τ 8.44 and 8.56, respectively. Consequently, the signals in the pmr spectrum of **8** are

assigned as indicated in the figure. The stereochemical assignments of the substituent groups in **8** follow from the mode of formation of **8** (cf. ref 6).

An analogous photodecarbonylation occurs with the tetramethylepoxy ketone **10**: mp 85–86°; pmr (CDCl_3) aliphatic methyls at τ 9.27, 8.73, 8.49, and 8.39, bridgehead protons at τ 6.82 and 6.21, and an aromatic multiplet, τ 3.0–2.6, which is readily obtained by treatment of **9**⁸ with *m*-chloroperbenzoic acid. Comparable irradiation of **10** gives **11** in ca. 75% yield.⁹ The pmr



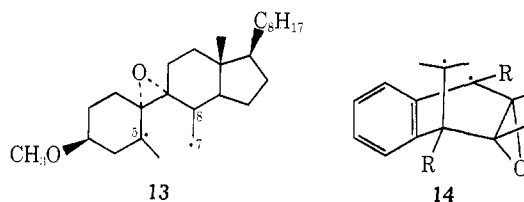
(CDCl_3) spectrum of **11** consists of three-proton singlets at τ 8.57, 8.49, and 8.48, a broad two-proton singlet at τ 6.81, a one-proton singlet at τ 6.15, a one-proton multiplet at τ 5.20, a broad one-proton singlet at τ 4.92, and a four-proton aromatic multiplet centered at τ 2.87. The pmr (CDCl_3) spectrum of the model epoxide **12**, prepared from 2,3-dimethyl-1,4-dihydronaph-



thalene,¹⁰ contains a six-proton singlet at τ 8.56, a broad four-proton singlet at τ 6.89, and an aromatic multiplet centered at τ 2.93.

Irradiation of acetone solutions of epoxy ketones **5** or **10** through Pyrex results in a much slower rate of disappearance of the epoxy ketones, and the formation of complex reaction mixtures.

Chambers and Marples have concluded from labeling studies that diradical **13** provides **2** by two hydrogen migrations, C-7 \rightarrow C-5 and C-8 \rightarrow C-7 (overall a formal 1,4-hydrogen shift), which may be consecutive in this order or synchronous.⁶ However, this mechanism does not account for the formation of **8** from **5** and **11** from **10**. Ostensibly, **8** and **11** result from diradical **14**



following formal 1,6-hydrogen shifts. Thus, it is apparent that the Chambers and Marples mechanism is not an exclusive route for the photodecarbonylation of β,γ -epoxy ketones.

Experimental Section

syn-7,8-Epoxy-1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]-oct-5-en-2-one (**5**).—A solution of 0.790 g (3.89 mmol) of 85%

(8) Ketone **9** was first prepared by T. Kakihana (M.S. Thesis, Michigan State University, 1966); experimental details are presented here.

(9) Monitoring the photoreaction by glpc indicated the formation of a minor photoproduct, which proved to be photolabile under the reaction conditions, and was not identified.

(10) G. Arich and S. Volpe, *J. Gas Chromatogr.*, **6**, 384 (1968).

m-chloroperbenzoic acid in 15 ml of methylene chloride was added during 15 min to an ice-cold stirred solution of 0.900 g (3.34 mmol) of **4** in 30 ml of methylene chloride. Stirring was continued in an ice bath for 1 hr and at room temperature for an additional 24 hr. Excess peracid was destroyed by the addition of 10% sodium sulfite until a test with starch-iodide paper was negative. The reaction mixture was washed with 5% sodium bicarbonate solution (3 × 50 ml), water (2 × 50 ml), and saturated sodium chloride solution (2 × 50 ml), and dried over anhydrous magnesium sulfate. Evaporation of the solvent provided an oil which was exhaustively evaporated of solvent at reduced pressure to give 0.900 g (89%) of **5**, which was recrystallized from pentane, mp 83–85°. The pmr spectrum is discussed in the text; ir (CCl₄) 2980, 1720, 1480, 1460, 1390, 1380, 1370, 1280, 1175, 1090, 1030, 1010, and 870 cm⁻¹; λ_{max}^{CHCl₃} 316 nm (ε 200), 305 (340), 295 (330), 282 (260), 271 (465), 264 (510), 258 (300), 227 (5000).

Anal. Calcd for C₁₈H₂₂O₂: C, 79.96; H, 8.20. Found: C, 79.89; H, 8.15.

Similarly, *syn*-7,8-epoxy-1,3,3,7,8-pentamethyl-4-methyl-*d*₃-5,6-benzobicyclo[2.2.2]oct-5-en-2-one (**6**) was prepared by epoxidation of 1,3,3,7,8-pentamethyl-4-methyl-*d*₃-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one⁶ and *syn*-7,8-epoxy-1,3,3,4,8-pentamethyl-7-methyl-*d*₃-5,6-benzobicyclo[2.2.2]oct-5-en-2-one (**7**) was obtained from 1,3,3,4,8-pentamethyl-7-methyl-*d*₃-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one.⁷

General Photolysis Procedure.—All irradiations were carried out with a 450-W Hanovia Type L mercury lamp with the light filtered through a Correx glass sleeve. The solution to be irradiated was placed in a quartz test tube, sealed with a serum cap, and attached to the outside of a water-cooled immersion well, 2–3 cm from the center of the mercury lamp. This apparatus was then placed in a water bath, which maintained the temperature of the solution between 15 and 20° during irradiation.

For each of the irradiations reported, a control experiment showed that no reaction occurred under comparable conditions in the dark.

Irradiation of Epoxy Ketone 5.—A solution of 100 mg of **5** in 10 ml of diethyl ether was irradiated through a Correx filter. The photolysis was monitored by glpc (10 ft × 0.25 in. FFAP column; 215°; 60 ml/min of helium). Irradiation led to a progressive decrease in the concentration of **5** (retention time 22.6 min) and an increase in the concentration of a photoproduct with a retention time of 10.2 min. This photoproduct reached a maximum concentration after 225-min irradiation, and further irradiation for 75 min produced only a slight decrease in its concentration. After 5-hr irradiation, no more starting material remained. Glpc and pmr analysis with internal standards indicated that the photoproduct was obtained in ca. 95% yield. Purification of the photoproduct by glpc (above conditions) provided a colorless oil, epoxide **8**. The pmr spectrum is discussed in the text; ir (CCl₄) 2980, 2940, 1640, 1495, 1450, 1370, 1175, 1150, 1120, 1100, 1060, 1040, 900, and 870 cm⁻¹. The major peaks in the mass spectrum [*m/e* 242 (M⁺)] are at 199 and 157.

Anal. Calcd for C₁₇H₂₂O: C, 84.25; H, 9.15. Found: C, 84.37; H, 9.17.

3,3,7,8-Tetramethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (9).⁸—A solution of anthranilic acid (4.5 g, 33 mmol) in acetone (40 ml) was added during 1 hr to a solution of 3,4,6,6-tetramethyl-2,4-cyclohexadienone¹¹ (3.28 g, 21.8 mmol) and isoamyl nitrite (3.87 g, 33 mmol) in methylene chloride (80 ml). After an additional 1 hr at reflux, the solvent was evaporated and the residual brown oil was dissolved in ether (70 ml) and washed with 10% sodium hydroxide, then water, and finally dried over anhydrous sodium sulfate. Evaporation of the solvent provided an oil which was distilled to give 3.18 g (63%) of **9**, a pale yellow oil: bp 104–105° (0.5 Torr); pmr (CCl₄) three-proton singlets at τ 9.42, 8.86, 8.23, and 8.16, one-proton singlets at τ 6.60 and 5.98, and a four-proton aromatic multiplet centered at τ 2.88; ir (CCl₄) 1720, 1675, 1600, and 710 cm⁻¹; λ_{max}^{EtOH} 300 nm (ε 389), 273 (1100), 268 (1200), and 216 (8130). Treatment of **9** with hydroxylamine hydrochloride in ethanol-pyridine gave a crystalline oxime, mp 175–176° (from ethanol).

Anal. Calcd for C₁₆H₁₈NO: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.90; H, 7.94; N, 5.80.

***syn*-7,8-Epoxy-3,3,7,8-tetramethyl-5,6-benzobicyclo[2.2.2]octa-5-en-2-one (10).**—Epoxidation of **9** with *m*-chloroperbenzoic acid, according to the procedure described in detail for **4** → **5**, gave epoxy ketone **10**, mp 85–86° (from pentane). The pmr spectrum

is discussed in the text; ir (CCl₄) 2975, 2925, 1725, 1475, 1455, 1380, 1195, 1165, 1130, 1095, and 875 cm⁻¹.

Anal. Calcd for C₁₆H₁₈O₂: C, 79.31; H, 7.49. Found: C, 79.39; H, 7.44.

Irradiation of Epoxy Ketone 10.—A solution of 100 mg of **10** in 10 ml of diethyl ether was irradiated through a Correx filter. The photolysis was monitored by glpc (10 ft × 0.25 in. FFAP column; 210°; 60 ml/min of helium). Examination of the solution after 30-min irradiation showed a significant decrease in the concentration of **10** (retention time 25.9 min), the appearance of a main photoproduct (retention time 11.8 min), and a trace of another photoproduct (retention time 8.2 min). Continued irradiation led to a progressive decrease in the concentration of **10** and a progressive increase in the concentration of the photoproduct with retention time 11.8 min. A new photoproduct with retention time 6.2 min also appeared and further irradiation led to an increase in the concentration of this product at the expense of the compound with retention time 8.2 min. After 5-hr irradiation, no more starting material remained, and integration of the peak areas of the photoproducts showed their relative concentrations to be retention time 6.2 min (4.6%), 8.2 min (2.1%), and 11.8 min (93.3%). Pmr analysis with an internal standard of the photolysate indicated that the photoproduct with a retention time of 11.8 min was obtained in ca. 75% yield. This photoproduct was purified by glpc (above conditions) to provide a colorless oil, epoxide **11**. The pmr spectrum is discussed in the text; ir (CCl₄) 3075, 3010, 2970, 1640, 1495, 1450, 1385, 1245, 1170, 1145, 1080, 1010, 900, and 875 cm⁻¹.

Anal. Calcd for C₁₆H₁₈O: C, 84.07; H, 8.47. Found: C, 84.27; H, 8.49.

2,3-Epoxy-2,3-dimethyl-1,4-dihydronaphthalene (12).—Epoxidation of 2,3-dimethyl-1,4-dihydronaphthalene¹⁰ with *m*-chloroperbenzoic acid, according to the procedure described in detail for **4** → **5**, gave **12**. The pmr spectrum is discussed in the text.

Anal. Calcd for C₁₂H₁₄O: C, 82.72; H, 8.10. Found: C, 82.84; H, 8.07.

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Registry No.—**4**, 17384-73-5; **5**, 41498-90-2; **8**, 41498-91-3; **9**, 22686-90-4; **9** oxime, 41498-21-9; **10**, 41498-92-4; **11**, 41498-93-5; **12**, 41498-22-0; 3,4,6,6-tetramethyl-2,4-cyclohexadienone, 14069-95-5; 2,3-dimethyl-1,4-dihydronaphthalene, 21564-72-7.

Photosensitized Oxygenations of Some Derivatives of Kaurenes

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The dye-sensitized photooxygenation of organic compounds, which has been studied extensively by many workers,² provides a smooth method for the specific

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