Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.97; H, 8.76.

2,2-Dimethyl-4-isopropyl-1,3-cyclobutanedione (IIIc) was obtained in 80% yield: mp 138–140 °C; ir (Me_2SO) 1612, 1742, and 3444 cm^{-1}; ir (KBr) 1759 cm^{-1}; NMR (Me_2SO) δ 0.98 (d, 6 H), 1.06 (s, 6 H), 2.24 (septet, 1 H), and 2.44 (s, 1 H); mass spectrum parent peak at *m/e* 154.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 70.03; H, 9.54.

4-*tert*-Butyl-2,2-dimethyl-1,3-cyclobutanedione (IIId) was obtained in 90% yield: mp 217 °C; ir (Me_2SO) 1633, 1739, and 3444 cm^{-1}; ir (KBr) 1724 cm^{-1}; NMR (Me_2SO) δ 1.12 (s, 15 H), 2.54 (s, 1 H); mass spectrum parent peak at *m/e* 8.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 71.66; H, 9.70.

General Procedure for Baeyer–Villiger Oxidation. The peroxyacetic acid was prepared by a standard procedure.[12] To 50 ml of $CHCl_3$ containing 0.015 mol of I or III was added dropwise at room temperature 0.05 mol of peracetic acid. The solution was stirred and the reaction monitored by VPC. After the disappearance of all the dione, the organic layer was separated and washed with dilute sodium carbonate solution and then dried over magnesium sulfate. The $CHCl_3$ was removed under reduced pressure and the β-keto-γ-lactone distilled.

α-Chloro-α,γ-dimethyl-β-keto-γ-valerolactone (Va). This lactone was obtained in 70% yield at 53–56 °C (0.05 mm): ir 1770 and 1809 cm^{-1}; NMR δ 1.52 (s, 3 H), 1.84 (s, 6 H); mass spectrum parent peak at *m/e* 176.

Anal. Calcd for $C_7H_9ClO_3$: C, 47.60; H, 5.14. Found: C, 47.33; H, 5.01.

α-Chloro-α-ethyl-γ-methyl-γ-valerolactone (Vb). This lactone was distilled at 61–63 °C (0.05 mm) in 55% yield: ir 1770 and 1809 cm^{-1}; NMR δ 0.99 (t, 3 H), 1.56 (s, 3 H), 1.72 (s, 3 H), 2.18 (q, 2 H); mass spectrum parent peak *m/e* 190.

Anal. Calcd for $C_8H_{11}ClO_3$: C, 50.40; H, 5.82. Found: C, 50.79; H, 5.62.

$\alpha,\alpha,\delta,\delta$-Tetramethyl-$\beta$-keto-$\gamma$-caprolactone (VI) was obtained in 15% yield at 66–67 °C (0.05 mm): ir 1739 and 1802 cm^{-1}; NMR δ 1.06 (s, 9 H), 1.20 (s, 3 H), 1.26 (s, 3 H), and 4.24 (s, 1 H); mass spectrum parent peak at *m/e* 184.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.22; H, 8.69. Found: C, 65.32; H, 8.99.

General Procedure for Diazomethane Reaction with Cyclobutanediones. The diazomethane was prepared by a standard procedure.[13] To 0.01 mol of I or III in 50 ml of ether was added 0.03 mol of diazomethane in ether at petroleum ether–dry ice temperature. Upon warming to room temperature, the reaction solution was stirred for 3 days. The solvent was removed under reduced pressure and the product vacuum distilled.

4-Chloromethyl-2,2,4-trimethyl-1,3-cyclobutanedione (VII). This dione was distilled at 44–46 °C (0.025 mm) in 20% yield: ir 1770 cm^{-1}; NMR δ 1.36 (s, 6 H), 2.00 (s, 3 H), and 4.24 (s, 2 H); mass spectrum parent peak at *m/e* 174.

3-Methoxy-2,2,4-trimethylcyclobutenone (VIIIa). An 87% yield was obtained at 38–39 °C (0.05 mm): ir 1616 and 1750 cm^{-1}; NMR δ 1.11 (s, 6 H), 1.60 (s, 3 H), and 4.11 (s, 3 H); mass spectrum parent peak at *m/e* 140.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.94; H, 8.74.

4-Ethyl-3-methoxy-2,2-dimethylcyclobutenone (VIIIb). An 85% yield was obtained at 45–47 °C (0.05 mm): ir 1616 and 1750 cm^{-1}; NMR δ 1.14 (s, 6 H), 1.40 (t, 3 H), 2.20 (q, 2 H), and 3.94 (s, 3 H); mass spectrum parent peak at *m/e* 154.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.02; H, 9.09. Found: C, 69.82; H, 9.11.

3-Methoxy-2,2-dimethyl-4-isopropylcyclobutenone (VIIIc). This compound was obtained at 52–54 °C (0.05 mm) in 80% yield: ir 1616 and 1750 cm^{-1}; NMR δ 0.92 (s, 6 H), 1.04 (s, 6 H), 2.28 (s, 1 H), and 3.96 (s, 3 H); mass spectrum parent peak *m/e* 168.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.19; H, 9.99.

4-*tert*-Butyl-3-methoxy-2,2-dimethylcyclobutenone (VIIId). A 90% yield was obtained at 45–47 °C (0.025 mm): ir 1626 and 1752 cm^{-1}; NMR δ 1.1 (s, 9 H), 1.3 (s, 6 H), and 4.0 (s, 3 H); mass spectrum parent peak *m/e* 182.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.89. Found: C, 71.81; H, 9.97.

General Procedure for Sodium Borohydride Reduction. To a stirred solution of 0.015 mol of VIII in 100 ml of methanol was slowly added sodium borohydride until the reduction was complete as evidenced by VPC. The solvent was removed and the saturated alcohol vacuum distilled.

3-Methoxy-2,2,4-trimethylcyclobutanol (Xa). This alcohol was distilled at 35–37 °C (0.025 mm) in nearly quantitative yield: ir 3334 cm^{-1}; NMR δ 0.09 (s, 3 H), 1.08 (s, 3 H), 1.12 (s, 3 H), 1.78 (q, 1 H), 2.41 (s, 1 H), 2.54 (d, 1 H, J_{trans} = 7 Hz), and 2.82 (d, 1 H, J_{trans} = 7 Hz).

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.84; H, 11.29.

4-*tert*-Butyl-3-methoxy-2,2-dimethylcyclobutanol (IXd). This alcohol was obtained at 62–63 °C (0.05 mm) in quantitative yield: ir 3334 cm^{-1}; NMR δ 0.96 (s, 9 H), 0.98 (s, 3 H), 1.04 (s, 3 H), 1.64 (s, 1 H), 1.90 (dd, 1 H), 3.22 (s, 3 H), 3.47 (d, 1 H, J_{cis} = 10 Hz), and 3.76 (d, 1 H, J_{trans} = 7 Hz).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.86; H, 11.83. Found: C, 71.22; H, 11.97.

Registry No.—Ia, 56513-93-0; Ib, 56513-92-9; Ic, 56513-95-2; Id, 56513-91-8; IIa, 58548-55-3; IIb, 58548-56-4; IIc, 56513-99-6; IIIa, 58548-57-5; IIIb, 58548-58-6; IIIc, 58548-59-7; IIId, 58548-60-0; Va, 58548-61-1; Vb, 58548-62-2; VI, 58548-63-3; VII, 58548-64-4; VIIIa, 13083-31-3; VIIIb, 58548-65-5; VIIIc, 58548-66-6; VIIId, 58548-67-7; IXd, 58548-68-8; Xa, 58548-69-9.

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Photochemistry of Diphenylcyclopropanecarboxylic Acid Derivatives

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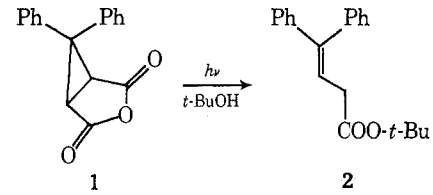
Although the photoextrusion of carbenes by arylcyclopropanes is a general reaction, the importance of this process relative to others available to excited cyclopropanes is highly structure dependent.[1] We wish to report here our observations concerning this process in two diphenylcyclopropanecarboxylic acid derivatives.

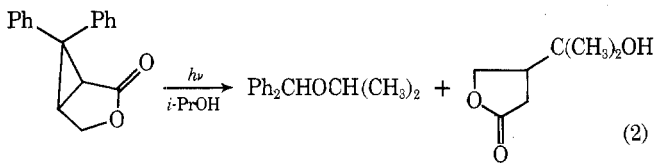
Results and Discussion

Irradiation of the anhydride **1**[2] in *tert*-butyl alcohol with Vycor-filtered light for 4 h afforded (1,1-dimethyl)ethyl 4,4-diphenylbut-3-enoate (**2**) in 57% yield at 10% conversion. No (1,1-dimethyl)ethylbenzhydryl ether[3] could be detected. In contrast to this, a similar irradiation of the lactone **3** in isopropyl alcohol produced benzhydryl isopropyl ether (**4**) in 80% yield and the hydroxy lactone **5** in 75% yield at 11% conversion. In each case sensitization with acetone using Corex-filtered light was unsuccessful. The structures of the photoproducts were confirmed by comparison with independently synthesized, previously reported materials.[3–5]



(1)

1 2



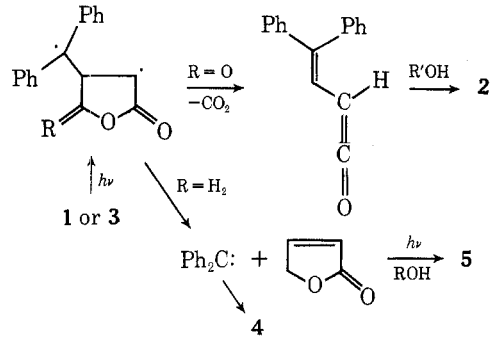
(2)

3 4 5

Both of these reactions can be rationalized in terms of cyclopropane bond homolysis to produce trimethylene diradicals.[1,6] In the case of the anhydride, cycloelimination of carbon dioxide would then lead to the formation of an unsaturated ketene which should capture solvent to give the observed product. This is depicted in Scheme I.

The diradical derivable from 3 cannot eliminate CO_2 in the same fashion and thus may fragment to diphenylcarbene and the unsaturated lactone. This olefin is known[5] to add isopropyl alcohol photochemically in the manner depicted in Scheme I.

Scheme I



It should be noted that the evidence presented here does not require the intermediacy of a diradical. Hixson[7] has shown that a cyclopropane closely related to those described here fragments stereospecifically to produce the diphenylcarbene and an olefin in a process that, as in these reactions, originates only from the singlet excited state.

Experimental Section

General. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Proton magnetic resonance spectra were recorded on a Varian Associates T-60 instrument with tetramethylsilane as the internal standard. Irradiations were conducted using a 450-W Hanovia lamp in a quartz immersion well. Irradiation solutions were deoxygenated by bubbling nitrogen through them for 1 h before and then during irradiation. Isopropyl alcohol was distilled from magnesium just before use. *tert*-Butyl alcohol was distilled from potassium.

Irradiation of 6,6-Diphenyl-3-oxabicyclo[3.1.0]hexane-2,4-dione (1). A solution of 284 mg (1.07 mmol) of 1[2] in 330 ml of *tert*-butyl alcohol was irradiated for 4 h using a Vycor filter. After solvent removal the NMR spectrum of the photomixture indicated that the major component of the mixture was starting material, but that there was an additional absorption signal at δ 3.07. This material was dissolved in 100 ml of ether, stirred with 100 ml of water, and the organic layer washed with 10% sodium carbonate solution. The ether solution was dried and the solvent removed. The residue was chromatographed on a 2.5 × 190 cm column slurry packed in hexane; 50-ml fractions were collected. Elution was accomplished with 250 ml of hexane and then 1 l. each of 5 and 10% ether–hexane. Fractions 27–34 contained 25 mg of a yellow oil. Attempted crystallization of this oil from chloroform–hexane afforded 18 mg (57% based on recovered starting material) of a clear oil. This material was identified as (1,1-dimethyl)ethyl 4,4-diphenylbut-3-enoate by comparison with the authentic ester synthesized from the known acid.[4] The photoproduct ester was dissolved in cyclohexane containing several drops of sulfuric acid and a white precipitate formed in several minutes. This solid was recrystallized from cyclohexane to afford 13 mg of 4,4-diphenylbut-3-enoic acid, mp 116–117 °C, mmp with authentic[4] acid 116–118 °C (lit.[4] mp 114–115 °C). The NMR spectrum ($CDCl_3$) is δ 9.8 (br, 1 H, COOH), 7.1–6.9 (m, 10 H), 5.97 (triplet, 1 H, J = 6 Hz), 3.07 (doublet, 2 H, J = 6 Hz). The spectrum of the *tert*-butyl ester was identical with the exception of the absence of the acid proton resonance and the presence of the *tert*-butyl group absorption at δ 1.43 (singlet, 9 H). Acidification of the sodium carbonate wash afforded 271 mg of a mixture of the *cis*- and *trans*-3,3-diphenyl-1,2-cyclopropanedicarboxylic acids.[2] A similar irradiation of 1 using 10.0 ml of acetone (0.136 mol) as a sensitizer and a Corex light filter gave no detectable reaction in a 12-h irradiation.

6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-2-one (3). A solution of 1.80 g (9.28 mmol) of diphenyldiazomethane[8] in 100 ml of dry benzene was added dropwise over 0.5 h to a solution of 2.00 g (23.8 mmol) of 2 (5*H*)-furanone[9] in 100 ml of dry benzene at room temperature. This material was heated at reflux for 4 h and the solvent removed in vacuo. The oily product mixture was chromatographed on a 2.5 × 87.5 cm column of Florisil slurry packed in hexane; 50-ml fractions were collected. Elution was with 500 ml of hexane and 500-ml portions of 2, 4, 8, and 15% ether–hexane. Fractions 23–25 contained 610 mg of an oil. Crystallization from ether–hexane afforded 458 mg (20%) of 3, mp 136–137 °C. Spectral data were uv (CH_3OH) 274 nm (ϵ 34), 268 (59), 261 (60), 254 (49); NMR ($CDCl_3$) δ 2.80 (multiplet, 2 H), 4.25 (m, 2 H), 7.1 (m, 10 H); MS (50 ev) *m/e* (rel intensity) 250 (31) (M^+), 205 (100), 165 (68); ir (KBr) 1775 (sh), 1750 (sh), 1195, 700 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.88; H, 5.69.

Irradiation of 6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-2-one (3). A solution of 301 mg (1.20 mmol) of 3 in 330 ml of isopropyl alcohol was irradiated for 4 h using a Vycor filter. After solvent removal most of the starting material was crystallized from ether–hexane, 268 mg, mp 135–137 °C. The residue was then separated by gas chromatography (156 °C, 20% SE-30 on firebrick in a 5 ft × 0.25 in. column, flow rate 60 ml He/min) to give 24 mg of isopropyl benzhydryl ether (4) (retention time 2.7 min) and 15 mg of 4-(1′-hydroxy-1′-methylethyl)-4,5-dihydro-2(3*H*)-furanone (5) (retention time 21 min). The identities of these materials were confirmed by the superimposability of their ir and NMR spectra upon those of independently synthesized materials. The ether 4 was made by a standard method[10] and the hydroxy lactone prepared by the irradiation of 2(5*H*)-furanone[9] as reported by Ohga and Matsuo.[5] A similar irradiation of 3 in which 10 ml of the solvent was replaced by acetone as a sensitizer afforded no reaction after 12 h of irradiation.

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Registry No.—1, 26844-85-9; 2, 58540-89-9; 2 free acid, 7498-88-6; 3, 58540-90-2; diphenyldiazomethane, 883-40-9; 2(5*H*)-furanone, 497-23-1.

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A Phosgeneless Synthesis of Diaryl Carbonates

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The production of diaryl carbonates most often involves at some point the use of extremely toxic phosgene. In this