slowly. This mixture was subsequently stirred at room temperature for 2 h, after which it was diluted with 400 ml of water and the product was isolated by extraction with ether. Evaporative distillation afforded 1.34 g (62%) of unsaturated ester **3b:** bp 78–82 °C (bath temperature, 0.1 mm) [lit.[14] bp 136–138 °C (16 mm)]; λ_{max} (film) 1735 (C=O), 1650 (C=C), 1605, 1500, 1165, 1035, 900, 740, 700 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.41 (s, 5 aromatic H's), 4.82 (broad s, CH_2=C), 4.15 (quartet, J = 7 Hz, OCH_2CH_3), 1.73 (s, vinyl CH_3), 1.16 ppm (t, J = 7 Hz, OCH_2CH_3).

Ethyl 2-Phenyl-4-methyl-4,5-epoxypentanoate (5b). Using the procedure described above for the preparation of **5a**, epoxide **5b** was obtained in 74% yield as a colorless oil: λ_{max} (film) 1730 (C=O), 1160, 1030, 700 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.43 (s, 5 aromatic H's), 4.19 (quartet, J = 7 Hz, OCH_2CH_3), 1.28 (s, CH_3), 1.17 ppm (t, J = 7 Hz, OCH_2CH_3). Since this oily epoxide (**5b**) proved in our hands to be unstable to vacuum distillation, no attempt was made to further purify it.

1-Phenyl-2-oxo-5-methyl-3-oxabicyclo[3.1.0]hexane (10). Treatment of 0.600 g (2.56 mmol) of crude epoxide **5b** with 3.1 mmol of sodium hydride in 50 ml of anhydrous dimethyl sulfoxide using the procedure described above for the preparation of alcohol **8a** afforded, after chromatography on Florisil and recrystallization from 10% ether–hexane, 160 mg (34%) of bicyclic lactone **10:** mp 63–64 °C; λ_{max} (KBr) 1765 (C=O), 1165, 1075, 1010, 755, 695 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.54 (s, C_6H_5), 4.41 (AB quartet, peaks at 4.60, 4.45, 4.37, 4.22, CH_2O), 1.54 (AB quartet, peaks at 1.70, 1.62, 1.45, 1.37, 2 cyclopropyl H's), 1.09 ppm (s, CH_3). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.56; H, 6.43. Found: C, 76.65; H, 6.64.

Ethyl 3,3-Dimethyl-4-pentenoate (3c). A mixture of 1.718 g (19.94 mmol) of 3-methyl-2-buten-1-ol,[7] 26 ml of triethyl orthoacetate,[7] and 74 mg (1 mmol) of propionic acid was heated at 140° for 36 h under conditions that allowed distillative removal of ethanol through a Vigreux column. After cooling this solution, it was poured into 40 ml of 5% (v/v) aqueous sulfuric acid and this mixture was subsequently stirred (with cooling in a water bath to maintain the temperature at or below 25 °C) for 5 min to hydrolyze the excess triethyl orthoacetate. Extraction of the crude product with pentane, followed by chromatography on Florisil (elution with hexane–5% ether), afforded 2.204 g (71%) of ester **3c:** bp 35–45 °C (bath temperature, 0.10 mm); λ_{max} (film) 3120, 1735 (C=O), 1635 (C=C), 1230, 1200, 1120, 1025, 905 cm^{-1}; δ_{Me_4Si} (CCl_4) 6.17–4.77 (complex pattern, 3 vinyl H's, peaks at 6.17, 5.99, 5.86, 5.69, 5.10, 5.08, 5.00, 4.97, 4.81, 4.79, and 4.77), 4.08 (quartet, J = 7.0 Hz, OCH_2CH_3), 2.21 (s, CH_2C=O), 1.22 (triplet, J = 7.0 Hz, OCH_2CH_3), 1.13 ppm (s, CH_3CCH_3). Anal. Calcd for $C_9H_{16}O_2$: C, 69.21; H, 10.33. Found: C, 69.03; H, 10.29.

Ethyl 4,5-Epoxy-3,3-dimethylpentanoate (5c). A solution containing 1.214 g (7.78 mmol) of unsaturated ester **3c** and 10 mmol of *m*-chloroperbenzoic acid[7] in 20 ml of anhydrous ether was refluxed for 18 h. After washing the ether layer with 5% aqueous sodium hydroxide and saturated brine, epoxide **5c** was isolated in the usual manner[12] in 95% yield: bp 45–55 °C (bath temperature, 0.10 mm); λ_{max} (film) 1730 (C=O), 1260, 1230, 1115, 1030 cm^{-1}; δ_{Me_4Si} (CCl_4) 4.12 (quartet, J = 7.0 Hz, OCH_2CH_3), 2.80 (triplet, J = 3.5 Hz, oxirane CH), 2.54 (d, J = 3.5 Hz, oxirane CH_2), 2.23 (s, CH_2C=O), 1.26 (t, J = 7.0 Hz, OCH_2CH_3), 1.0 (s, CH_3), 0.97 ppm (s, CH_3). Anal. Calcd for $C_9H_{16}O_3$: C, 62.78; H, 9.37. Found: C, 62.66; H, 9.36.

Ethyl 2-Hydroxymethyl-3,3-dimethylcyclopropanecarboxylate (8c). A solution of 944 mg (5.49 mmol) of ester **5c** and 2.0 ml of hexamethylphosphoramide in 10 ml of anhydrous tetrahydrofuran was added dropwise to a solution of 11 mmol of lithium diisopropylamide[9] in 50 ml of anhydrous tetrahydrofuran at −70 °C. After stirring this mixture at −70 °C for 7 h, the reaction was quenched by pouring the solution into 50 ml of saturated aqueous ammonium chloride solution. Extraction of the crude product with ether, followed by chromatography on Florisil (elution with 1:1 ether–hexane), afforded 378 mg (40%) of cyclopropanoid **8c:** bp 60–80 °C (bath temperature, 0.20 mm); λ_{max} (film) 3470 (OH), 1722 (C=O), 1205, 1170, 1110, 1025 cm^{-1}; δ_{Me_4Si} (CCl_4) 4.08 (quartet, J = 7 Hz, OCH_2CH_3), 3.57 (dd, variable broadening, CH_2OH), 1.25 (t, J = 7 Hz, OCH_2CH_3), 1.21 ppm (s, 2 CH_3's). Anal. Calcd for $C_9H_{16}O_3$: C, 62.78; H, 9.37. Found: C, 62.59; H, 9.47.

Ethyl *trans*-2-Formyl-3,3-dimethylcyclopropanecarboxylate (9d). Oxidation of alcohol **8c** was effected using the method developed by Ratcliffe and Rodehorst,[10] affording the corresponding aldehyde (**9d**) in 90% yield: bp 50–63 °C (bath temperature, 0.08 mm); >94% pure by VPC analysis,[15] oven temperature 155 °C, retention time 3.0 min; λ_{max} (film) 2775 (CHO), 1725 (ester C=O), 1700 (HC=O), 1225, 1170, 1100 cm^{-1}; δ_{Me_4Si} (CCl_4) 9.60 (d, J = 2.0 Hz, CHO), 4.12 (quartet, J = 7.0 Hz, OCH_2CH_3), 2.39 (d, J = 2.0 Hz, CHCHO), 2.37 (s, $CHCO_2CH_2CH_3$), 1.35 (s, CH_3), 1.30 (s, CH_3), 1.27 ppm (t, J = 7.0 Hz, OCH_2CH_3). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51: H, 8.29. Found: C, 63.23; H, 8.50.

Acknowledgments. The authors are grateful to Research Corporation for financial support of this work. In addition, the assistance of Douglas O. Olsen and Mark A. Turner in some of the experimental work directed toward the synthesis of *trans*-chrysanthemic acid is acknowledged.

Registry No.—**1a**, 101-81-5; **1b**, 101-97-3; **1c**, 79-09-4; **2**, 563-47-3; **3a**, 33925-52-9; **3b**, 14815-83-9; **3c**, 7796-72-7; **5a**, 54949-91-6; **5b**, 57496-91-0; **5c**, 57496-92-1; **8a**, 27067-50-1; **8c**, 40427-26-7; **9d**, 38692-37-4; **9f**, 827-90-7; **15**, 57496-93-2; 3-methyl-2-buten-1-ol, 556-82-1.

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(12) Reactions were carried out under a nitrogen atmosphere. Unless indicated otherwise, the isolation of reaction products was accomplished by pouring the mixture into water or saturated brine and extracting thoroughly with the specified solvent. Anhydrous magnesium sulfate was used to dry the combined extracts, and the solvent was removed on a rotary evaporator under reduced pressure. Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. Melting points were determined on a Fisher-Johns block and are corrected. The NMR spectra were recorded with a Varian A-60 NMR spectrometer and infrared spectra were obtained using either a Beckman Acculab 1 or a Perkin-Elmer 700 A spectrophotometer. Microanalyses were performed by MicroTech Laboratories, Inc., Skokie, Ill.
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Efficient Syntheses of Barrelene and Nenitzescu's Hydrocarbon[1]

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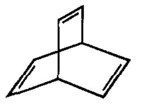
Received September 12, 1975

Since their initial syntheses, the hydrocarbons barrelene (bicyclo[2.2.2]octa-2,5,7-triene, **1**)[2,3] and Nenitzescu's hydrocarbon (tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene, **2**)[4,5] have been of interest since they are of theoretical interest, themselves, and since they offered ready access to some $(CH)_8$ and $(CH)_{10}$ hydrocarbons, respectively.[6] The studies related to **1** and **2** have been hampered owing to the inaccessibility of sizable quantities of the hydrocarbons. For example, the syntheses of barrelene were accomplished in less than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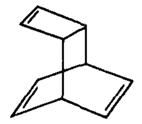
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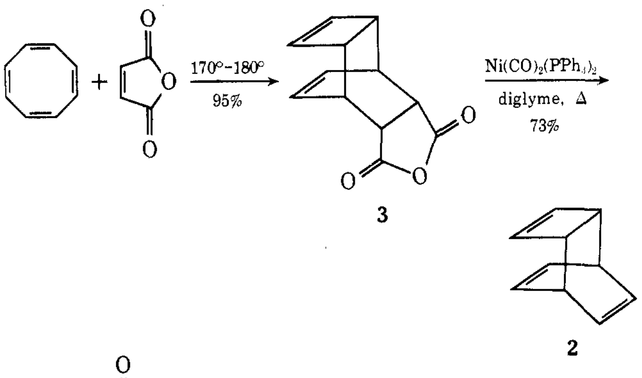
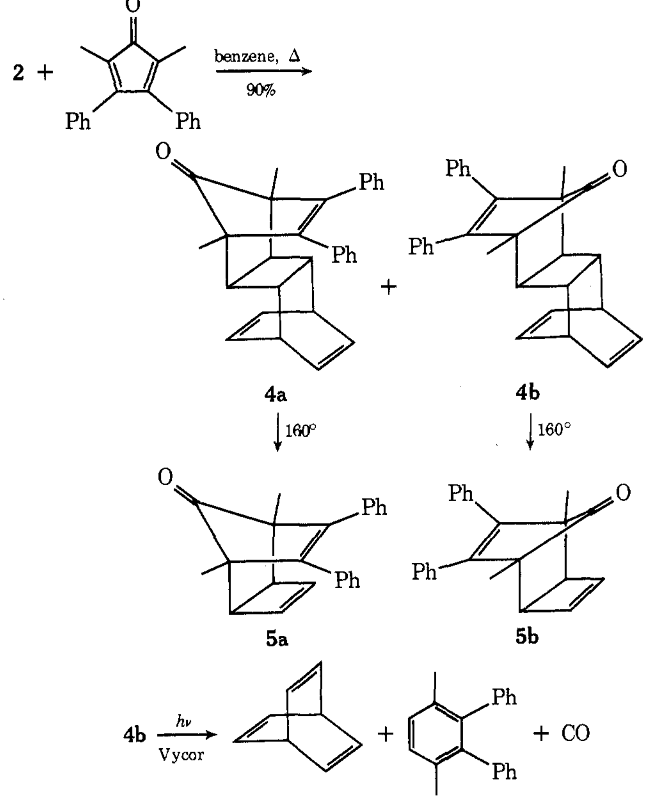
2% overall yield[2,3] and the early preparations of Nenitzescu's hydrocarbon suffered from a low yield in the final lead tetraacetate oxidative bisdecarboxylation step[4] or in the ability to scale up other oxidative bisdecarboxylation reaction sequences.[5]

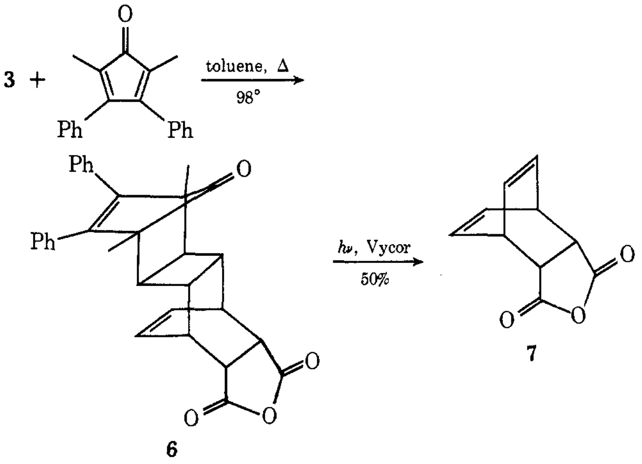
Recently, the synthesis of **2** was accomplished via a six-step sequence in an overall yield from cyclooctatetraene of 36%.[7] The syntheses of related compounds in the laboratory using a [4 + 2] cycloreversion reaction to transfer a four-carbon unit from one moiety to another[8] led us to examine again the synthesis of **1** and **2** by a more efficient method. Using a related two-carbon transfer reaction (1,2-photoaromatization)[9] the latter compound could serve as a precursor of **1**.





The Diels-Alder adduct **3**, prepared in 95% yield by allowing cyclooctatetraene and maleic anhydride to react at 170-180°, was oxidatively bisdecarboxylated with dicarbonylbis(triphenylphosphine)nickel[10] in refluxing diglyme to give tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (**2**) in 73% yield on a 20-25-g scale.[11] The overall yield for this two-step preparation from cyclooctatetraene was 69%.

The [4 + 2] cycloaddition reaction between **2** and 2,5-dimethyl-3,4-diphenylcyclopentadienone was accomplished in refluxing benzene and gave in 90% yield a mixture of endo and exo isomers **4a** and **4b**; the exo isomer was the predominant product and could be obtained pure in 70% yield. Upon heating to 160°, this pure isomer **4b** yielded the known exo ketone **5b** in 90% yield. The exo isomer **4b** upon ultraviolet irradiation (Vycor filter) in dry tetrahydrofuran, after vacuum transfer, gave a solution of barrelene (**1**), contaminated with a trace of benzene and cyclooctatetraene;[12] the yield of barrelene was 50%. As in all the earlier preparations, pure hydrocarbon was obtained by preparative gas chromatography. The yield of barrelene from cyclooctatetraene was 24%.



Other obvious variations in the reaction sequence were investigated. For example, the Diels-Alder reaction between anhydride **3** and the dienone proceeded in near quantitative yield to give **6**. This adduct upon 1,2 photoaromatization gave **7** in 50% yield. This "benzene Diels-Alder" product, **7**, is a crystalline solid and is stable in the cold. In solution the product slowly undergoes a retro-Diels-Alder reaction ($t_{1/2}{}^{25°}$ ~30 h) to yield benzene and maleic anhydride. Alternatively, when the adduct **6** was subjected to electrolytic oxidative bisdecarboxylation, the diene **4b** was obtained in only 33% yield. The thermal process using dicarbonylbis(triphenylphosphine)nickel could not be used, since as discussed above, the first formed product **4b** was thermally unstable under the reaction conditions.

Experimental Section

Unless otherwise noted, the following general conditions were used in all reactions. Infrared spectra were recorded using either a Perkin-Elmer 137 Infracord or a 237 grating spectrometer. NMR spectra were obtained with a Varian T-60 spectrometer and tetramethylsilane as an internal standard. Mass spectral analyses and elemental analyses were obtained from The Analytical Laboratory, College of Chemistry, University of California, Berkeley, Calif.

Tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (2). In a 500-ml, three-necked, round-bottomed flask equipped with a mechanical stirrer were placed *endo*-tricyclo[4.2.2.0^{2,5}]deca-3,5-diene-7,8-dicarboxylic anhydride (**3**, 22.5 g, 0.11 mol),[13] dicarbonyl bis(triphenylphosphine)nickel (87 g, 0.14 mol),[14] and anhydrous diglyme (200 ml). The solution was heated under vigorous reflux (bath temperature 200°, nitrogen atmosphere) for 3.5 hr, during which time the color of the solution changed from yellow-green to dark black.[15] The reaction was cooled to room temperature (some unreacted nickel catalyst precipitated), the condenser was replaced by a distillation head, and the diglyme and hydrocarbons were distilled under aspirator vacuum (bp 60-65°) into a dry ice cooled trap. An additional 50 ml of diglyme was added to the residue and distilled. The combined distillate was poured into water (1000 ml) and the mixture extracted with three 150-ml portions of isopentane. The hydrocarbon phase was washed three times with water (the complete removal of the diglyme established by GC analysis) and the isopentane solution dried (Na_2SO_4). The solvent was distilled at atmospheric pressure using a 12-cm vacuum-jacket spiral wire filled column. The residue was distilled through a short-path still, bp 72–73° (18 mm), to yield 10.55 g (73%) of 98% (GC) pure hydrocarbon. The product displayed spectral characteristics identical with the reported values.[4,5]

***exo*-4,7-Dimethyl-5,6-diphenylpentacyclo[8.2.2.$1^{4,7}.0^{2,9}.0^{3,8}$]pentadeca-5,11,13-trien-15-one (4b).** In a 250-ml, round-bottomed flask equipped with a reflux condenser were placed tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (**2**, 10.15 g, 0.078 mol), 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer (20.0 g, 0.04 mol),[14] and dry benzene (100 ml). The solution was refluxed with magnetic stirring under a nitrogen atmosphere until the red color disappeared (~40 h) and cooled to room temperature, and ether (75 ml) was added. The white precipitate was filtered, washed with cold ether, and dried under reduced pressure at 25° to yield 21.1 g (70%) of exo isomer **4b**. An analytical sample was recrystallized from CCl_4–MeOH: mp 182–184° dec; NMR ($CDCl_3$) δ 1.19 (s, 6), 1.72–1.93 (m, 4), 3.62 (m, 2), 6.26–6.58 (overlapping triplets, apparent quintet, 4, J = 4 Hz), 6.78–7.30 (m, 10); ir (KBr) 696, 722, 760, 781, 809, 1395, 1440, 1755, and 2930 cm^{-1}; mass spectrum *m/e* 390 (M^+), 362 (M^+ – CO), 284 (M^+ – CO – benzene), 258.

Anal. Calcd for $C_{29}H_{26}O$: C, 89.19; H, 6.71. Found: C, 88.96; H, 6.76.

The filtrate was concentrated to a viscous oil, which was dissolved in hot CCl_4 (25 ml), and diluted with hot absolute EtOH (100 ml). The solution was rotary evaporated to 60 ml, the precipitate filtered, and the solid washed with EtOH. The filtrate was further concentrated to yield a product of lesser purity. A total of 7.1 g (22%) of product was obtained from the ethanolic solution, and these crops were enriched in the endo isomer: NMR ($CDCl_3$) δ 1.34 (s, 6), 1.88–2.30 (m, 4), 3.50–3.94 (m, 2), 6.25 (t, 2, J = 3.5 Hz), 6.51 (t, 2, J = 3.5 Hz), 6.85–7.32 (m, 10).

Bicyclo[2.2.2]octa-2,5,7-triene (1). To a quartz irradiation well equipped with a magnetic stirrer and a dry ice condenser was added a solution of **4b** (7.80 g, 20 mmol) in dry tetrahydrofuran (125 ml) and the solution was purged with dry nitrogen for 1 h. The solution was irradiated through a Vycor filter with a Hanovia 450-W lamp and the progress of the reaction followed by TLC (10% EtOAc–90% ligroin). After a 6-h period only traces of starting material remained and the irradiation was terminated. The reaction solution was transferred to a 250-ml, round-bottomed flask, the solution freeze–thaw degassed (five cycles, 25 μ), and the volatile material vacuum transferred to a 250-ml, round-bottomed flask cooled in liquid nitrogen; a thick yellow residue remained in the distillation flask. An additional 20 ml of tetrahydrofuran was added to the residue, and the vacuum transfer repeated. The combined tetrahydrofuran solution was concentrated by distillation through a 40-cm spinning-band column at atmospheric pressure to leave 7.26 g of solution (10.7 mol % barrelene by NMR analysis, yield 1.07 g, 51%) which contained benzene and cyclooctatetraene as trace contaminants. Pure barrelene was isolated by preparative gas chromatography (15 ft × 0.25 in., 2.5% SE-30, 120°) and a neat sample displayed spectral properties identical with the literature values.[2,3]

***exo*-1,6-Dimethyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-one (5b).** A sublimer containing **4a** (100 mg, 0.256 mmol) was heated at 160° under aspirator vacuum for 2 h. The white sublimate was collected, yield 70 mg (87%) of **5b**, and was resublimed under identical conditions: mp 132–135°;[16] NMR (CCl_4) δ 1.19 (s, 6), 3.09 (s, 2), 6.52 (s, 2), 6.88–7.32 (m, 10);[17] ir (CCl_4) 699, 848, 891, 907, 928, 970, 1010, 1070, 1170, 1185, 1280, 1370, 1445, 1485, 1770, 2900, and 3000 cm^{-1}; mass spectrum *m/e* 312 (M^+), 286 (M^+ – C_2H_2), 284, (M^+ – CO, base peak), 258.

Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.37; H, 6.29.

***exo*-4,7-Dimethyl-5,6-diphenylpentacyclo[8.2.2.$1^{4,7}.0^{2,9}.0^{3,8}$]pentadeca-5,13-dien-15-onedicarboxylic Acid Anhydride (6).** A suspension of crude *endo*-tricyclo[4.2.2.$0^{2,5}$]deca-3,9-diene-7,8-dicarboxylic acid anhydride (12.2 g, 0.06 mol), 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer (15.7 g, 0.03 mol), and 100 ml of toluene was heated under reflux for 24 h; the bright red color of the monomeric dienone gradually disappeared. The suspension was cooled in an ice bath, and the product filtered. To the filtrate there was added 100 ml of ether and a second crop of crystals was obtained. The combined crops were dried under vacuum: yield 27.6 g (98%); mp 278–280°; NMR ($CDCl_3$) δ 1.20 (s, 6), 2.02 (broad s, 4), 3.01 (t, 2, J = 2 Hz), 3.35 (m, 2), 6.45 (t, 2, J = 4 Hz), 6.80–7.30 (m, 10); ir (KBr) 750, 809, 915, 1085, 1220, 1770, and 1850 cm^{-1}; mass spectrum *m/e* 462 (M^+), 434 (M^+ – CO), 258.

Anal. Calcd for $C_{31}H_{26}O_4$: C, 80.50; H, 5.67. Found: C, 80.71; H, 5.48.

Bicyclo[2.2.2]octa-2,5-diene-7,8-dicarboxylic Anhydride (7). A solution of **6** (924 mg, 2 mmol) in dry tetrahydrofuran (30 ml) was placed in a Vycor tube fitted with a stopcock, the tube was cooled in ice water in a transparent quartz Dewar flask, and the solution was degassed with nitrogen. At ice temperature, the solution was irradiated for 9 h in a Rayonet reactor using 254-nm light sources. A small amount of solid material was filtered, and the solution treated twice with small portions of ligroin and the resulting solids removed. Finally, a 25-ml portion of ligroin was added and the flocculent precipitate filtered and dried (0°, vacuum) to give 190 mg (54%) of material of about 90% purity (NMR analysis): mp 70–80° dec; NMR ($CDCl_3$) δ 3.20 (t, 2, J = 1.5 Hz), 4.12 (m, 2), 6.54 (t, 2, J = 3.5 Hz); ir ($CHCl_3$) 824, 914, 930, 960, 1010, 1080, 1230, 1295, 1345, 1775, 1845, 2920, and 3020 cm^{-1}.

A small amount of **7** was recrystallized by dissolving it in a minimal amount of tetrahydrofuran at room temperature, followed by the addition of 4 volumes of ether. The resulting solution was chilled for 12 h and the crystalline precipitate was filtered (~30% recovery), mp 70–80% (dependent upon heating rate).

Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 68.14; H, 4.83.

Registry No.—**1**, 500-24-3; **2**, 21604-76-2; **3**, 51447-09-7; **4a**, 57496-75-0; **4b**, 57526-53-1; **5b**, 30450-25-0; **6**, 57496-76-1; **7**, 57496-77-2; 2,5-dimethyl-3,4-diphenylcyclopentadienone, 26307-17-5.

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(17) The endo isomer was produced along with the exo isomer when a mixture of the pentacyclic ketones was pyrolyzed, but the endo isomer was never isolated in pure form. The new NMR bands attributed to it occurred at δ 1.26 (s, 6), 2.96 (s, 2), 6.06 (s, 2), and 6.83–7.26 (m, 10).

Oxidation of Secondary Alcohols with Ozone[1]

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Received October 15, 1975

The ozonation of alcohols has received only scattered attention throughout the literature.[2] Primary interest has been a mechanistic interpretation of the oxidation process. However, since we[1,3] and others[2] have noted fairly rapid