characteristic retention times. The acetophenones were not actually isolated; GC product peacks with the expected retention times were assumed to correspond to these products which necessarily accompany the alkenes. Light intensity for quantum yield measurements was measured by parallel irradiation of 0.1 M valerophenone actinometers[17] and equalled 0.064 einstein L^{-1} h^{-1}.

Acknowledgment. This work was supported by NSF Grants No. CHE-76-11892 and -79-10831. M.J.T. thanks the Institute of General Medical Sciences of the NIH for a postdoctoral fellowship (No. CM57549-01).

Registry No. 1-OCF_3, 79619-25-3; 1-H, 1009-14-9; 1-OCH_3, 1671-76-7; 1-SCH_3, 42916-75-6; 2-SCF_3, 79631-89-3; *p*-(trifluoromethoxy)benzonitrile, 332-25-2; *p*-(trifluorothiomethoxy)benzonitrile, 332-26-3.

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4,7,7-Trimethyl-*cis*-bicyclo[3.3.0]oct-3-en-2-one: A Potentially Useful Synthon for Triquinane Natural Products

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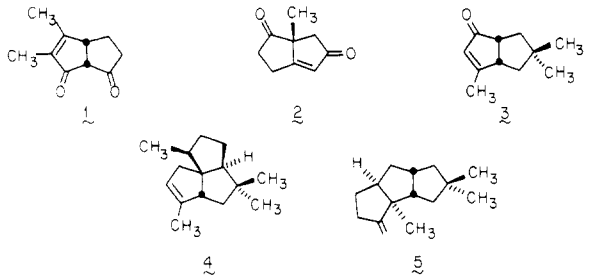
Received August 12, 1981

The rapidly growing number of structurally interesting and biologically active polyquinane (polycyclopentanoid) natural products[2] has prompted considerable interest in new methodology for the construction of condensed five-membered ring systems. Because the availability of functionalized bicyclo[3.3.0]octane building blocks could greatly facilitate the elaboration of more complex target molecules, the design of expedient synthetic routes to such intermediates has been actively pursued. The recent reports detailing pathways to 1[3] and 2[4] are exemplary. Herein we describe the preparation of title ketone 3 by a new scheme which begins with 4,4-dimethylcyclohexanone (6), a readily available substance.[5] The relationship of 3 to senoxydene (4),[6] hirsutene (5),[7] and their more structurally embellished congeners such as pentalenolactone E[8] and coriolin[9] is apparent.



With but one exception,[10] previous methods of five-ring annulation do not lead to fused cyclopent-3-en-2-ones.[2] In addition, it is doubtful that 3,3-dimethylcyclopentanone could be transformed regiospecifically into the desired synthon.[11] These considerations prompted us to examine the base-promoted ring contraction of a suitably substituted cyclohexanone derivative in the hope that the pendant groups could subsequently be crafted into the cyclopentenone moiety.

Carbomethoxylation of 6 with dimethyl carbonate and a mixture of sodium and potassium hydrides[12] produced 7 in 89% yield (Scheme I). Although new techniques are available for the preparation of 2-isopropylidenecycloalkanones,[13] our experience has been that the procedure originally described for the synthesis of pulegone[14] is both operationally simpler and more efficient in this instance. Thus, ketalization of 7 and treatment with methylmagnesium iodide led in excellent yield to the crystalline tertiary carbinol 8. This intermediate underwent direct conversion to 9 (82.5% yield) when heated in aqueous acidic methanol.

The salient feature of the impending ring contraction was the Favorskii rearrangement. Extensive studies have been made of the bromination and base-induced isomerization of pulegone.[15,16] However, the reaction of 9 with Br_2 in acetic acid proved sluggish and rather unpredictable; significant amounts of unreacted starting material were invariably recovered. A substantial improvement was made upon adaptation of the conditions of Marx and Norman[17] which involve slow addition of the halogen to a cold (−10 °C), buffered ($NaHCO_3$) ethereal solution of the α,β-unsaturated ketone. The dibromide was then directly added to methanolic sodium methoxide solution and left to stir at room temperature overnight. In a typical experiment, a 2:1 ratio of 10 and 9 was obtained and efficiently separated by high-pressure liquid chromatography (Waters Prep 500).

The conversion of 10 to bicyclic lactone 11, achieved simply by heating with hydrochloric acid in aqueous methanol, afforded colorless crystalline product in 82% yield. In agreement with Eaton's general findings,[18] 11 was conveniently isomerized to 3 upon heating (50 °C) in 8% phosphorus pentoxide–methanesulfonic acid solution. Interestingly, no evidence for the presence of the internal conjugated enone was detected under these cyclization conditions.

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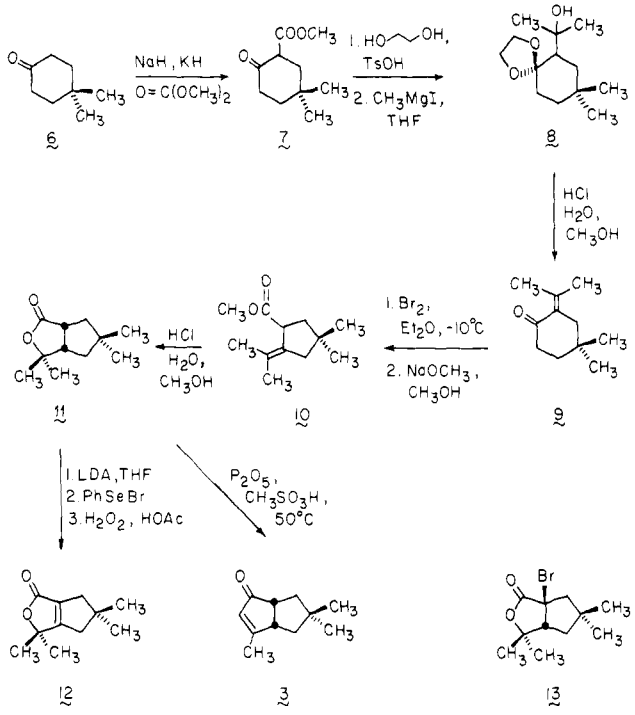
Scheme I



For use in various natural product syntheses, it could be desirable to functionalize **11** prior to acid-catalyzed rearrangement. Toward this end, its anion was condensed with phenylselenyl bromide[19] and the resulting α-phenylselenolactone was subjected to oxidation with 30% hydrogen peroxide. The planar-symmetric nature of unsaturated lactone **12** is clearly indicated by its ^{1}H NMR spectrum (in $CDCl_3$) which features only three sharp singlets at δ 2.32 (4 H), 1.46 (6 H), and 1.25 (6 H). In like fashion, generation of the anion of **11** followed by 1,2-dibromoethane quench[20] produces the bromo lactone **13** in 61% yield.

The relatively short route to **3** developed herein is noteworthy for the clean positional control of the carbonyl group and flanking double bond which is achieved. Additional applications of this scheme and further work with **3** itself are planned.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrometer. The ^{1}H NMR spectra were determined with Varian T-60 and EM-390 instruments, and apparent splittings are given in all cases. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative VPC purifications were achieved with Varian Aerograph Model A-90-P3 instruments equipped with thermal conductivity detectors. Microanalyses were determined by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

2-(Carbomethoxy)-4,4-dimethylcyclohexanone (7). Into a 500-mL three-necked flask was placed 10.2 g of 50% sodium hydride–oil suspension. While under nitrogen, the solid was washed 3 times with dry toluene and 3 times with anhydrous tetrahydrofuran (solvent removed by syringe). A solution of dimethyl carbonate (17 mL) in dry tetrahydrofuran (50 mL) was added dropwise and the stirred mixture was heated to reflux. Approximately 2 mL of a solution of **6**[5] (9.0 g, 71 mmol) in 20 mL of tetrahydrofuran was slowly added. At this point, a previously washed slurry of potassium hydride (0.6 g) in 9 mL of the same solvent was added. While the reaction mixture was being heated to reflux, the remaining ketone solution was added over 45 min. Heating was continued for 1.5 h and the flask was cooled in an ice bath. A solution of acetic acid (75 mL) and saturated brine (100 mL) was added, followed by ether (250 mL) and solid sodium bicarbonate. The layers were separated, and the aqueous phase was extracted with ether (2 × 100 mL). The combined organic layers were washed with brine, dried, and evaporated. Distillation of the residue gave 11.67 g (89%) of **7** as a colorless oil: bp 55–61 °C (0.3 torr); IR (CCl_4) 2900 (br), 1740, 1710, 1650, 1610, 1430,1350, 1275, 1220, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3 H), 2.27 (t, J = 7 Hz, 2 H), 2.02 (br s, 2 H), 1.40 (t, J = 7 Hz, 3 H), 0.97 (s, 6 H); mass spectrum, m/e calcd 184.1099, obsd 184.1106.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.27; H, 8.72.

Carbinol 8. A stirred solution of **7** (106 g, 0.58 mol), ethylene glycol (65 mL), and p-toluenesulfonic acid (0.5 g) in benzene (195 mL) was heated at reflux with azeotropic removal of water for 72 h. The product was partitioned between ether and water. The aqueous phase was extracted with ether (2 × 100 mL), and the combined organic layers were washed with sodium bicarbonate and brine solutions prior to drying and solvent evaporation. The residue was distilled to give 117.6 g (89.5%) of the ketal ester, bp 100–105 °C (0.35 torr). The colorless liquid solidified upon distillation: mp 39–44 °C; IR (CCl_4) 2980, 2900, 1750, 1550, 1440, 1370, 1350, 1200, 1070, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.9 (m, 4 H), 3.65 (s, 3 H), 2.85 (dd, J = 10 and 4 Hz, 1 H), 2.1–1.2 (series of m, 6 H), and 1.0 (s, 6 H); mass spectrum, m/e calcd 228.1361, obsd 228.1368.

To an ether solution containing approximately 0.51 mol of methylmagnesium iodide was added dropwise a solution of the ketal ester (43.0 g, 0.19 mol) in 120 mL of ether. After completion of the addition, the reaction mixture was heated at reflux for 2 h, cooled in ice, and treated with a solution of ammonium chloride (85.5 g) in water (190 mL). Additional water was added to dissolve the inorganic salts, the layers were separated, and the aqueous phase was extracted with ether (2 × 150 mL). The combined organic layers were washed with brine, dried, and evaporated. There was obtained 40.55 g (94%) of **8** as a colorless solid: mp 65–68 °C (from petroleum ether); IR (CCl_4) 3510, 2950, 1450, 1390, 1350, 1190, 1170, 1110, 1050, 940 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.66 (s, 1 H), 3.96 (m, 4 H), 2.2–1.35 (series of m, 7 H), 1.2 (s, 3 H), 1.15 (s, 3 H), 0.98 (s, 3 H), 0.92 (s, 3 H); mass spectrum, m/e calcd 228.1725, obsd 228.1732.

Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.24; H, 10.59.

2-Isopropylidene-4,4-dimethylcyclohexanone (9). A solution of **8** (26.96 g, 0.12 mol), concentrated hydrochloric acid (2.2 mL), water (100 mL), and methanol (166 mL) was heated at reflux with stirring for 2 h, cooled, and neutralized with solid sodium bicarbonate. The major portion of the methanol was evaporated under reduced pressure, water (50 mL) was added, and the mixture was extracted with ether (100 mL). The aqueous layer was further extracted with ether (2 × 100 mL), and the combined oranic layers were washed with brine, dried, and evaporated. Distillation of the residue afforded 16.35 g (82.5%) of **9** as a colorless oil: bp 47–49 °C (0.75 torr); IR (CCl_4) 2940, 2840, 1685, 1615, 1450, 1360, 1275, 1125 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.4 (t, J = 6 Hz, 2 H), 2.30 (s, 2 H), 1.95 (s, 3 H), 1.75 (s, 3 H), 1.65 (t, J = 6 Hz, 2 H), 1.1 (s, 6 H); mass spectrum, m/e calcd 166.1358, obsd 166.1362.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.21; H, 10.97.

1-(Carbomethoxy)-2-isopropylidene-4,4-dimethylcyclopentane (10). A mixture of **9** (5.0 g, 30 mmol) and sodium bicarbonate (1 g) in ether (30 mL) was blanketed with nitrogen and cooled to −10 °C. During 30 min, bromine (5 g, 30 mmol) was added and the reaction mixture was stirred for an additional hour and filtered. The filtrate was added to a solution of sodium methoxide in methanol (prepared from 2.5 g of sodium and 70 mL of methanol) which was stirred for 12 h and poured into a mixture of dilute hydrochloric acid and ice. The product was extracted into ether (3 × 100 mL). The combined organic layers were washed with saturated sodium bicarbonate and brine solutions, dried, and evaporated. The residual oil (5.07 g), consisting of a mixture of **9** and **10**, was separated into its components by high-pressure liquid chromatography on a Waters Prep 500 in-

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strument (silica gel, elution with 2% ethyl acetate in petroleum ether). There was isolated 1.36 g (27%) of **9** and 2.13 g (50% based on recovered starting material) of **10** as a colorless oil: IR (CCl_4) 2940, 2890, 1735, 1460, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.65 (s, 3 H), 2.22 (s, 2 H), 2.05–1.6 (m, 3 H), 1.64 (s, 3 H), 1.55 (s, 3 H), 1.10 (s, 3 H), 0.86 (s, 3 H); mass spectrum, *m/e* calcd 196.1463, obsd 196.1458.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.20; H, 10.24. Found: C, 72.85; H, 10.12.

Cyclization of 10. A solution containing **10** (2.13 g, 11 mmol), 8.5 mL of concentrated hydrochloric acid, 25 mL of methanol, and 4 mL of water was heated at the reflux temperature for 8 h. After the solution cooled, most of the methanol was removed under reduced pressure and the residue was partitioned between ether (75 mL) and water (50 mL). The aqueous phase was extracted with ether (2 × 75 mL), and the combined organic layers were washed with saturated sodium bicarbonate and brine solutions prior to drying and solvent evaporation. There was obtained 1.62 g (82%) of **11** as a brown oil which was purified by silica gel high-pressure liquid chromatography (elution with 6% ethyl acetate in petroleum ether). The pure lactone was a colorless crystalline solid: mp 42–43 °C; IR (CCl_4) 2950, 2860, 1770, 1450, 1190, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.25 (m, 1 H), 2.75 (m, 1 H), 1.85 (m, 2 H), 1.6 (s, 2 H), 1.5 (s, 3 H), 1.4 (s, 3 H), 1.15 (s, 3 H), 1.0 (s, 3 H); mass spectrum, *m/e* calcd ($M^+ - CH_3$) 167.1072, obsd 167.1066.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.32; H, 9.95.

Selenation–Oxidation of 11. A solution of **11** (200 mg, 1.10 mmol) in dry tetrahydrofuran (4 mL) was added to a cold (−78 °C) lithium diisopropylamide solution [prepared from diisopropylamine (0.32 mL, 2.6 mmol) and *n*-butyllithium (0.86 mL of 1.55 m in hexane, 1.30 mmol) by stirring for 10 min at −20 °C] and the mixture was stirred for 30 min. Phenylselenyl bromide (300 mg, 1.10 mmol) dissolved in tetrahydrofuran (6 mL) was added and the mixture was stirred at −78 °C for 2 h before being poured into ice-cold dilute hydrochloric acid. The aqueous phase was extracted with ether (3 × 50 mL), and the combined organic layers were washed with saturated sodium bicarbonate and brine solutions prior to drying. Solvent evaporation left an oil (220 mg) from which the selenide was obtained by preparative TLC on silica gel plates. In addition to the product (90 mg, 25%) there was recovered 25 mg of **11**: IR (CCl_4) 3300, 2960, 2280, 1730, 1580, 1390, 1260, 1160, 1140, 1020, 950, 900, 680 cm^1; ^1H NMR ($CDCl_3$) δ 7.75–7.15 (m, 5 H), 2.75 (t, J = 8 Hz, 1 H), 2.0 (s, 2 H), 1.64 (s, 3 H), 1.62–1.5 (m, 2 H), 1.32 (s, 3 H), 1.05 (s, 3 H), 0.98 (s, 3 H); mass spectrum, *m/e* calcd 338.0785, obsd 338.0777.

To a solution of the phenylseleno lactone (34.1 mg, 0.10 mmol) in carbon tetrachloride (15 mL) was added a 4:1:4 mixture of water/acetic acid/30% hydrogen peroxide (v/v/v, 4.5 mL). The biphasic mixture was heated at reflux for 7.5 h and poured into saturated sodium bicarbonate solution (25 mL) admixed with dichloromethane (25 mL). The layers were separated, and the organic phase was washed with 25-mL portions of water, dilute hydrochloric acid, water and brine. Following drying and solvent evaporation, there was obtained 10.5 mg (60%) of **12** as a colorless crystalline solid: mp 65–69 °C; IR (CCl_4) 2960, 1770, 1290, 1330 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.32 (s, 4 H), 1.46 (s, 6 H), 1.25 (s, 6 H); mass spectrum, *m/e* calcd 180.1150, obsd 180.1157.

Bromination of 11. To a cold (−78 °C) solution of the lithium enolate of **11** (300 mg, prepared as above) was added 3 mL of 1,2-dibromoethane. The reaction mixture was stirred at room temperature for 2 h, evaporated under reduced pressure, and treated with water. The aqueous mixture was extracted with ether (3 × 50 mL). The usual workup gave an orange oil (550 mg) which was purified by preparative TLC chromatography on silica gel (elution with 20:1 petroleum ether/ethyl acetate). There was obtained 260 mg (61%) of **13** as an off-white solid: mp 71–75 °C; IR (CCl_4) 2960, 2860, 1760, 1460, 1385, 1370, 1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.15 (dd, J = 12 and 6 Hz, 1 H), 2.35 (m, 2 H), 1.7 (s, 3 H), 1.55 (s, 2 H), 1.35 (s, 3 H), 1.20 (s, 3 H), 1.05 (s, 3 H); mass spectrum, *m/e* calcd 245.0178, obsd 245.0186.

4,7,7-Trimethyl-*cis*-bicyclo[3.3.0]oct-3-en-2-one (3). Into a solution of phosphorus pentoxide (4.5 g) in methanesulfonic acid (57 g), prepared by heating with stirring at 80 °C under nitrogen, was added lactone **11** (400 mg, 2.2 mmol) in small portions. The dark reaction mixture was heated at 50 °C for 48 h and added dropwise to water (150 mL). The resulting aqueous suspension was extracted with dichloromethane (6 × 25 mL), and the combined organic layers were washed successively with sodium bicarbonate solution (30 mL), water (30 mL), and brine (30 mL). Drying and solvent evaporation left a brown oil (298 mg) which was filtered through a silica gel plug (6.3% ethyl acetate in petroleum ether) to give 238 mg (70%) of **3**. The analytical sample was obtained by VPC (2 ft × 0.25 in. 5% SE-30 on Chromosorb G, 150 °C): IR (CCl_4) 2950, 1700, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.5 (s, 1 H), 3.4–2.8 (m, 2 H), 2.02 (s, 3 H), 2.0–1.1 (m, 4 H), 1.03 (s, 6 H); mass spectrum, *m/e* calcd 164.1201, obsd 164.1199.

Acknowledgment. We are indebted to the National Institutes of Health (Grant GM-28468) and Eli Lilly Co. for financial support of this research.

Registry No. **3**, 53874-09-2; **6**, 4255-62-3; **7**, 50388-51-7; **7** (ethylene ketal ester), 79618-60-3; **8**, 79618-61-4; **9**, 79618-62-5; **10**, 79618-63-6; **11**, 79618-64-7; **11** (phenylseleno lactone), 79618-65-8; **12**, 79618-66-9; **13**, 79618-67-0; methyl iodide, 74-88-4.

Preparation of Bicyclo[3.3.0]oct-1-en-3-one and Bicyclo[4.3.0]non-1(9)-en-8-one via Intramolecular Cyclization of α,ω-Enynes

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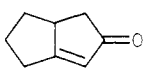
Received May 14, 1981

The presence of the bicyclo[3.3.0]octane ring system in a variety of biologically active natural products has generated considerable interest in the synthesis of its functionalized derivatives. In particular, two recent reports have described syntheses of enone **1**, a compound whose



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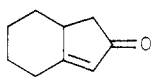
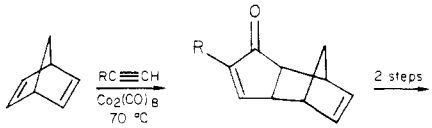


2

preparation has proved to be unexpectedly challenging.[1,2] We report here exceptionally simple syntheses of both **1** and its homologue **2**, syntheses that are unique in that they allow the preparation of these ketones *directly from acyclic starting materials*, without the need for prior formation of monocyclic intermediates.

The syntheses make use of the cobalt carbonyl promoted cocyclization of alkynes, alkenes, and carbon monoxide, a reaction first reported by Pauson and co-workers in 1973. The reaction utilizing norbornadiene[3,4] as the alkene provides good yields of products which, we have shown, are readily converted into simple cyclopentenone derivatives (eq 1).[5] Unfortunately, unstrained alkenes are consider-



50–60% 60–90% (1)

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