using benzene–chloroform to give **8** (0.15 g), **2** (1.24 g), and **15** (0.187 g).

15: mp 131–132 °C; ir (KBr) 1785, 1720 cm^{-1}; NMR ($CDCl_3$) δ 4.07 (1 H, d, J = 6.0 Hz), 3.70 (4 H, s, COOMe and 1 H), 3.37 (3 H, s, OMe), 3.2–2.6 (5 H, m), 1.2–1.83 (3 H, m).

Anal. Calcd for $C_{14}H_{16}O_5$: C, 67.73; H, 6.50. Found: C, 67.76; H, 6.47.

B. A solution of **2** (2.0 g) and TTN (3.1 g) in methanol (30 ml) was refluxed for 24 h. Workup gave **2** (0.925 g), **8** (0.505 g), and **15** (0.22 g).

Reaction of 16 with Silver Acetate. A. A mixture of **16** (0.4 g) and silver acetate (0.2 g) in acetic acid (20 ml) was refluxed for 2 h. The reaction mixture was filtered for precipitated silver salts, and the solvent was evaporated by reduced pressure. The residue was subjected to SGC using chloroform–benzene to give a mixture of **18** and **19** (0.31 g), which could not be separated by SGC. The mixture consisted of a 1:1 ratio as evidenced by HLC analysis, which was recrystallized from benzene–*n*-hexane to give **18** and **19.**

18: mp 120–120.5 °C; ir (KBr) 1760, 1740 cm^{-1}; NMR ($CDCl_3$) δ 4.80 (1 H, dd, J = 2.0 and 8.0 Hz), 4.65 (1 H, t, J = 2.0 Hz), 3.70 (3 H, s, COOMe), 3.20 (1 H, m), 2.3–2.9 (7 H, m), 2.00 (3 H, s, OAc).

Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.57; H, 5.70.

19: mp 138–139 °C ir (KBr) 1770, 1740, 1720 cm^{-1}; NMR ($CDCl_3$) δ 5.00 (1 H, s), 4.42 (1 H, d, J = 7.0 Hz), 3.37 (3 H, s, COOMe), 3.4–2.7 (4 H, m), 2.3–1.8 (2 H, m), 2.06 (3 H, s, OAc), 1.68 (2 H, m).

Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.54; H, 5.70.

B. A mixture of **16** (1.92 g) and silver acetate (0.96 g) in acetone (20 ml) and water (20 ml) was refluxed for 30 h. Workup gave **16** (0.34 g) and a mixture of **20** and **21** 0.7 g). The mixture consisted of a 1:1 ratio as evidenced by HLC analysis, which could not be separated.

Acetolysis of 17. A solution of **17** (0.44 g) and sodium acetate (0.09 g) in acetic acid (20 ml) was heated at 170 °C in a sealed tube for 36 h. Workup gave a mixture of **18** and **19** (0.25 g).

Reaction of 20 and 21 with Chromic Anhydride. To a mixture of chromic anhydride (0.5 g) and pyridine (5 g) a mixture of **20** and **21** (0.7 g) was added. After stirring for 24 h, the mixture was diluted with water and extracted with chloroform. The organic solvent was dried over sodium sulfate and then evaporated by reduced pressure. The residue was subjected to SGC using chloroform to give **25** (0.18 g). Compound **20** was recovered from the reaction mixture, which was treated with chromic anhydride in acetic acid; to a solution of **20** (0.1 g) in acetic acid (20 ml) chromic anhydride (0.03 g) was added. The mixture was stirred for 4 h. After dilution with water, the reaction mixture was extracted with chloroform. Evaporation of the solvent gave **22** (0.03 g).

20: mp 140–141 °C; ir (KBr) 3420, 1730 cm^{-1}; NMR ($CDCl_3$) δ 4.83 (1 H, dd, J = 8.0 and 2.0 Hz), 4.07 (1 H, m, changed to triple by D_2O, J = 3.0 Hz), 3.73 (3 H, s, COOMe), 3.20 (1 H, m), 2.9–2.5 (7 H, m, 1 H exchangeable by D_2O), 2.2 (1 H, m).

Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.04. Found: C, 62.49; H, 5.78.

22: mp 203–205 °C; ir (KBr) 1805, 1770, 1740 cm^{-1}; NMR (Me_2SO-d_6) δ 4.98 (1 H, dd, J = 9.0 and 2.0 Hz), 3.63 (3 H, s, COOMe), 3.5–2.5 (8 H, m). Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.80; H, 4.82.

25: mp 187–189 °C; ir (KBr) 1770, 1720 cm^{-1}; NMR ($CDCl_3$) δ 4.70 (1 H, d, J = 6.5 Hz), 3.73 (3 H, s, COOMe), 3.6–2.8 (4 H, m), 2.5–2.0 (4 H, m).

Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.98; H, 5.02.

Reaction of 20 and 21 with Acetic Anhydride. A solution of a mixture of **20** and **21** (1:1 ratio) (0.1 g) in acetic anhydride (1 ml) and pyridine (5 ml) was stirred for 24 h at room temperature. The solution was diluted with water and then extracted with chloroform. The extract was washed with 2 N hydrochloric acid and then with water. The organic solvent was dried over sodium sulfate and evaporated by reduced pressure to give **18** and **19** (total 0.15 g).

Reaction of 23 with Chromic Anhydride. To a solution of **23** (0.5 g) in acetic acid (20 ml), chromic anhydride (0.15 g) was added. Workup as described above gave **22** (0.374 g).

Registry No.—**1**, 51447-09-7; **2**, 35211-83-7; **4**, 58832-37-4; **5**, 58865-34-2; **6**, 58832-38-5; **7**, 58832-39-6; **8**, 58832-40-9; **9**, 58832-41-0; **10**, 58832-42-1; **11**, 58832-43-2; **12**, 58832-44-3; **13**, 58832-45-4; **14**, 58832-46-5; **15**, 58832-47-6; **16**, 58832-48-7; **18**, 58865-35-3; **19**, 58832-49-8; **20**, 58865-36-4; **21**, 58832-50-1; **22**, 58832-51-2; **25**, 58832-52-3; LTA, 546-67-8; *p*-nitrobenzoyl chloride, 122-04-3; TTA, 2570-63-0; TTN, 13746-98-0; silver acetate, 563-63-3; diacetoxy acetal of 2,4,6-cycloheptatriene, 58832-53-4; maleic anhydride, 108-31-6.

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Annulated Cyclopentadienone Ketals. A Route to 1,2-Bridged Norbornenes

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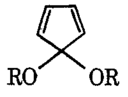
The preparation and properties of a new set of cyclopentadienone ketals are described. These annulated cyclopentadienone ketals are interesting theoretically and are useful in the synthesis of new types of polycyclic systems.

The ketals of cyclopentadienone (**1a–c**) are exceedingly reactive substances; Diels–Alder dimerization occurs very rapidly.[1] The dimethyl ketal **1a**, the least reactive of the set, dimerizes about 270 times faster than cyclopentadiene; the ethylene ketal **1c** dimerizes more than another 1000 times faster. A significant bathochromic shift in the ultraviolet absorption maximum of these dienes has been noted [cyclopentadiene, λ_{max}(pentane) 239 nm; **1a**, 270 nm; **1b**, 272 nm; **1c**, 280 nm] and is most probably related to these large changes in reactivity. The interactions of the cyclopentadiene π system with the nonbonding electrons of the ketal oxygens

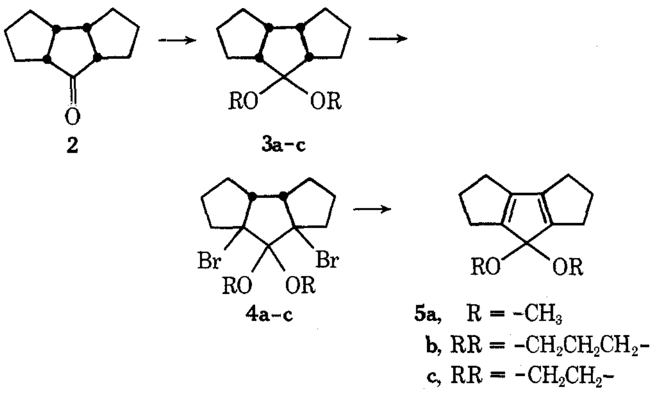


1a, R = $-CH_3$
b, RR = $-CH_2CH_2CH_2-$
c, RR = $-CH_2CH_2-$

are presumably the cause of these effects.[1,2] Unfortunately, the reactivity of these cyclopentadienone ketals has precluded the collection of other data (e.g., photoelectron spectra) important to understanding these interactions.

We wish to report now the preparation and isolation of a set of annulated cyclopentadienone ketals sufficiently stable to permit accumulation of the needed information and sufficiently symmetric and free of extraneous electronic effects to make this effort worthwhile. In addition, these new dienes offer interesting synthetic possibilities.

The tricyclic ketone **2** is readily available, as we describe elsewhere.[3] The ketals of this saturated ketone are preparable by standard acid-catalyzed reactions: the dimethyl ketal (**3a**) by reaction of **2** with excess trimethyl orthoformate; the propylene ketal (**3b**) and the ethylene ketal (**3c**) by reaction of **2** with the appropriate glycols. Each ketal reacts with 2 equiv of pyridinium hydrobromide perbromide (**3a** in methanol; **3b,c** in THF) at 5–15 °C to give the corresponding α,α'-dibromo ketal (**4a–c**). Dehydrobromination is effected directly by reaction under nitrogen with potassium *tert*-butoxide in Me_2SO at room temperature. The desired products are obtainable pure by repeated chromatography on silica gel and/or low-temperature crystallization. The propylene ketal **5b** melts at 79–80 °C; the ethylene ketal **5c**, at 78–80 °C. The dimethyl ketal **5a** has not been obtained crystalline.



2

3a–c

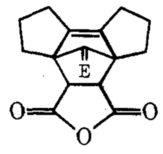
4a–c

5a, R = $-CH_3$
b, RR = $-CH_2CH_2CH_2-$
c, RR = $-CH_2CH_2-$

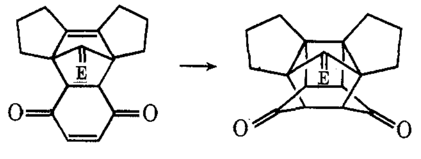
It is necessary to note that the dehydrobromination reactions **4** → **5** are not clean. Materials containing vinyl hydrogen, presumably formed by base-catalyzed double bond migrations, contaminate the crude reaction products. In the case of the ethylene ketal **5c**, on which we have concentrated our efforts, only a 25% yield of pure material could be obtained from the dehydrobromination mixture. This was sufficient for our purposes. No doubt, a better dehydrobromination procedure could be developed.

The ultraviolet absorption maximum of the carefully purified dimethyl (**5a**), propylene (**5b**), and ethylene (**5c**) ketals shifts from 294 to 297 to 304 nm with the change in ketal group. This parallels the shift noted for the unsubstituted ketals **1a–c**. The long-term stability of **5a–c** allows measurement of the ^{13}C NMR spectra. The chemical shifts of the olefinic carbon atoms do not change much from ketal to ketal: **5a**, δ 146.8, 150.7; **5b**, 146.4, 151.1; **5c**, 147.4, 150.6 ppm relative to internal Me_4Si.[4] This was unexpected and still seems odd. We had thought that the electronic perturbation of the diene system evident in the ultraviolet shift would also be apparent in the NMR.[6] The photoelectron spectral behavior of these new ketals is under study.

As we hoped, the reactivity of the diene ketals **5a–c** is substantially reduced from that of the parent system **1a–c** by the steric effects of the fused rings. However, these dienes are still quite reactive toward good dienophiles. For example, the ethylene ketal **5c** reacts quickly with maleic anhydride or with *p*-benzoquinone in boiling benzene to give the corresponding Diels–Alder adducts **6** and **7**. Interestingly, intramolecular photocyclization by irradiation of **7** in benzene produces the winged cage **8** in good yield. Compounds **6**, **7**, and **8** are the first examples of materials with such carbon skeletons. Attention is called in particular to the substantial strain introduced at the norbornene double bond in **6** and in **7** by the fused rings with termini at the vinyl and bridgehead carbon atoms.



6



7 8

(E = ethylene ketal)

Experimental Section

Proton magnetic resonance spectra were taken at 270 MHz on solutions in deuteriochloroform and are referenced to internal Me_4Si. Spectra were recorded for convenience on compressed scale (3 Hz/mm); therefore, quoted shifts are no better than ±0.02 ppm and coupling constants are ±1 Hz, sufficient accuracy for the purpose. Carbon magnetic resonance spectra were run at 22.63 MHz on solutions in deuteriochloroform using standard pulse techniques and white-noise decoupling. These spectra are also referenced to internal Me_4Si; chemical shifts are ±0.1 ppm. Infrared spectra were taken using Nujol mulls; positions of interesting absorptions are quoted ±5 cm^{-1}. The high-resolution mass spectrum of each characterized compound was recorded on an MS-9 spectrometer operating at 50 eV ionization voltage. Each compound exhibited a proper parent peak at *m/e* within 30 ppm of the expected value. Ultraviolet spectra were taken on solutions made up in carefully purified cyclohexane.

Ketals of *cis,syn,cis*-Tricyclo[6.3.0.0^{3,7}]undecan-2-one. Dimethyl Ketal (3a). A mixture of **2**[3] (3 g), trimethyl orthoformate (6 g), and *p*-toluenesulfonic acid (170 mg) was kept at room temperature for 14 h. Gas chromatographic analysis indicated complete disappearance of the ketone. Sodium methoxide (500 mg) was added to the reaction mixture. The suspension was added dropwise to well-stirred, 10% aqueous sodium carbonate (200 ml). This mixture was extracted with light petroleum ether (2 × 150 ml). The organic layer was washed with 10% aqueous sodium carbonate (3 × 100 ml) and dried over sodium carbonate. Removal of solvent in vacuo left an oil (2.8 g). In general, this crude ketal was used directly. The material is thermally labile. A small sample was purified by molecular distillation (~25 °C, 0.01 mm): ^{13}C NMR δ 112.4 (ketal carbon), 52.6 (junction), 50.6 ($-OCH_3$), 48.0 ($-OCH_3$), 44.3 (junction), 28.9 (two signals <2 Hz apart), and 27.3 ppm.

Propylene Ketal (3b). The ketone **2** (4 g), propylene glycol (8 g), and methanesulfonic acid (8 drops) were combined together in benzene (200 ml) and heated under reflux beneath a Dean-Stark trap for 3 days. The mixture was cooled, and sodium methoxide (3 g) was added with stirring. The reaction mixture was added dropwise to stirred, 10% aqueous sodium carbonate, and this mixture was extracted with hexane (2 × 200 ml). The extract was washed with 3% aqueous sodium carbonate and dried over sodium carbonate. The solution was concentrated under vacuum. Distillation of the residue gave a fraction (3.2 g), bp 102–105 °C (0.5 mm), better than 95% pure by GLC analysis on OV-225: ^{13}C NMR δ 109.6 (ketal carbon), 62.4 ($-OCH_2-$), 60.3 ($-OCH_2-$), 53.3, 43.9, 29.0, 28.5, 27.2, 25.8 ppm (the last is probably $-OCH_2CH_2CH_2O-$ based on its relative intensity).

Ethylene Ketal (3c). The ketone **2** (14.0 g), 28.0 g of ethylene glycol, and 4 drops of methanesulfonic acid were combined together in 200 ml of benzene and stirred under reflux beneath a Dean-Stark trap for 4 days. The mixture was cooled, and then added dropwise with rapid stirring to 10% aqueous sodium carbonate. The basic mixture was extracted with hexane (3 × 50 ml). The combined extract was washed with 3% aqueous sodium carbonate and dried over sodium carbonate. Removal of the solvent in vacuo left 15.7 g (88%) of **3c** which was used directly in the next step. A small sample was purified by molecular distillation under high vacuum at room temperature:

^{13}C NMR δ 119.1 (ketal carbon), 66.5 (–OCH_2–), 64.2 (–OCH_2–), 55.2, 44.9, 28.9, 28.4, and 27.1 ppm.

Bromination of the Ketals 3a–c (→ 4a–c). Pyridinium hydrobromide perbromide (50 g, 93% titre, 145 mmol) was added in small portions to a stirred solution of the ethylene ketal **3c** (15 g, 72 mmol) in 250 ml of dry THF at 5 °C. The reaction mixture was stirred at 5–10° for 1 h; the original orange color of the brominating agent discharged to yellow. After this time, pyridine (12 g) was added with vigorous stirring. The reaction mixture was then added slowly from a dropping funnel into 250 ml of 10% aqueous sodium carbonate solution stirred rapidly. This mixture was extracted with hexane (3 × 150 ml) The extract was washed with 3% aqueous sodium carbonate and dried over Na_2SO_4. Removal of solvent in vacuo gave 29 g of a brown oil containing traces of pyridine. The oil was kept under high vacuum for 24 h to remove most of the pyridine. Crude **4c** was then used directly in the next step.

Similar procedures were followed for the bromination of **3a** and **3b**. For **3a** → **4a**, methanol was substituted for THF; this is essential.

Tricyclo[6.3.0.0^{3,7}]undeca-1(8),3(7)-dien-2-one Ketals (5a–c). Ethylene Ketal (5c). The crude dibromo ketal **4c** (18.5 g) was dissolved in 50 ml of dry Me_2SO. This mixture was stirred rapidly under nitrogen at 15–20 °C as a solution of potassium *tert*-butoxide (22 g) in 200 ml of dry Me_2SO was added dropwise. Stirring at 15–20 °C was continued for 4 h. After this time, the mixture was poured into stirred, 10% aqueous sodium carbonate solution (200 ml). This mixture was extracted with ether (3 × 150 ml). The ether extract was washed with 3% aqueous sodium carbonate (3 × 50 ml), dried over sodium sulfate, and decolorized with Norit. Removal of the solvent in vacuo left 10 g of yellow oil. Crystallization from light petroleum ether at 0–10 °C gave 2.7 g of good **5c** (25%). Recrystallization from petroleum ether gave a pure product: mp 79–80 °C; ^1H NMR δ 4.10 (4 H, s) and 2.1–2.5 ppm (12 H); ^{13}C NMR δ 150.6 and 147.3 (vinyl carbons), 108.2 (ketal carbon), 65.2 (–OCH_2–), 27.6, 27.5, and 27.0 ppm; uv λ 304 nm (ε 1700).

Dimethyl (5a) and Propylene Ketal (5b). Similar procedures were followed for the dehydrobromination of **4a** and **4b**. The unsaturated ketals **5a** and **5b** were purified by column chromatography on silica gel using light petroleum ether/ethyl ether (85:15) as eluent. The propylene ketal **5b** could be purified to mp 78–80 °C by crystallization from mixed hexanes at −20 °C. Compound **5a:** ^{13}C NMR δ 150.7 and 146.8 (vinyl carbons), 104.7 (ketal carbon), 51.9 (–OCH_3), 29.7, 27.7, and 27.2 ppm; uv λ 294 nm (ε 1120). Compound **5b:** ^{13}C NMR δ 151.1 and 146.4 (vinyl carbons), 102.1 (ketal carbon), 63.1 (–OCH_2–), 30.7, 27.7, 26.9, and 25.7 ppm; uv λ 297 nm (ε 1800).

Diels–Alder Adducts from Ethylene Ketal 5c. Adduct 6 from Maleic Anhydride. A solution of maleic anhydride (50 mg, 0.51 mmol) and ketal **5c** (102 mg, 0.50 mmol) in 4 ml of benzene was refluxed for 4 h. The solvent was removed under vacuum, and the residue triturated with ether. The solid residue (110 mg, 73%) was reasonably pure adduct **6**, mp 234–237 °C. A purer sample was obtained by crystallization from acetonitrile: mp 238–240 °C; ^1H NMR δ 3.9 (4 H, center of symmetrical multiplet, ketal), 3.46 (2 H, s, ring junction), 2.2 (2 H, m), and 2.1–1.6 ppm (10 H); ^{13}C NMR δ 171.9 (anhydride carbonyl), 141.2 (vinyl), 69.5 (bridgehead?), 65.9 and 65.7 (–OCH_2–), 49.0 (junction), 28.5, 26.0, and 23.7 ppm (cyclopentane CH_2). The quaternary ketal carbon was not found in the ^{13}C NMR spectrum; its relaxation time is probably very long, a result of its isolation from CH units.

Adduct 7 from *p*-Benzoquinone. A solution of ketal **5c** (306 mg, 1.5 mmol) and *p*-benzoquinone (162 mg, 1.5 mmol) in 15 ml of benzene was refluxed for 21 h. The solvent was removed, and the residue chromatographed on silica gel. The 1:1 petroleum ether/ether eluate gave 260 mg (55%) of the desired adduct, which could be further purified by crystallization from mixed hexanes: mp 143–144 °C; ir 1672 cm^{-1}; ^1H NMR δ 6.61 (2 H, s), 3.95 (4 H, center of symmetrical ketal multiplet), 3.27 (2 H, s, junction), 2.2 (2 H, m), 2.1–1.6 ppm (10 H).

Photochemical Closure of 7 to 8. A solution of **7** (40 mg) in 0.5 ml of benzene was exposed to the output from a Hanovia 450-W mercury arc lamp filtered through Pyrex glass. The closure was followed by NMR. When nearly all of the vinyl hydrogen resonance signal of the starting material had disappeared, the irradiation was stopped. The solvent was removed under vacuum. The product was crystallized from benzene to give 30 mg (75%) of **8:** mp 153–155 °C; ir 1742 and 1765 cm^{-1}; ^1H NMR (C_6D_6) δ 3.39 (4 H, s), 2.84 (2 H, s), 2.26 (2 H, s), 1.84 (2 H, m), 1.67 (2 H, m), 1.44 (4 H, m), and 1.17 ppm (4 H, m).

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Registry No.—**2**, 58866-18-5; **3a**, 58881-35-9; **3b**, 58866-62-9; **3c**, 58866-63-0; **4a**, 58881-36-0; **4b**, 58866-64-1; **4c**, 58866-65-2; **5a**, 58866-66-3; **5b**, 58866-67-4; **5c**, 58866-68-5; **6**, 58866-69-6; **7**, 58866-70-9; **8**, 5866-71-0; trimethyl orthoformate, 149-73-5; propylene glycol, 504-63-2; ethylene glycol, 107-21-1; pyridinium hydrobromide perbromide, 39416-48-3; maleic anhydride, 108-31-6; *p*-benzoquinone, 106-51-4.

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cis,syn,cis-Tricyclo[6.3.0.0^{3,7}]undecane Ketones

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The synthesis of the first examples of compounds in the *cis,syn,cis*-tricyclo[6.3.0.0^{3,7}]undecane series is described. A preparatively useful synthesis of 1,1′-dicyclopentenyl ketone is given.

For our work on the synthesis of peristylane and dodecahedrane[1] we wanted to have available model systems containing three five-membered rings fused serially; that is, compounds in the tricyclo[6.3.0.0^{3,7}]undecane series (1). Examples with this carbon skeleton are rare; most that are known are derivatives of the natural product hirustic acid C (2)[2] or have been made along the way in the synthesis of that compound.[3] Hirustic acid has cis,anti,cis stereochemistry at the ring fusions. We required compounds in the more hindered cis,syn,cis series. To our knowledge, no preparations of such