^{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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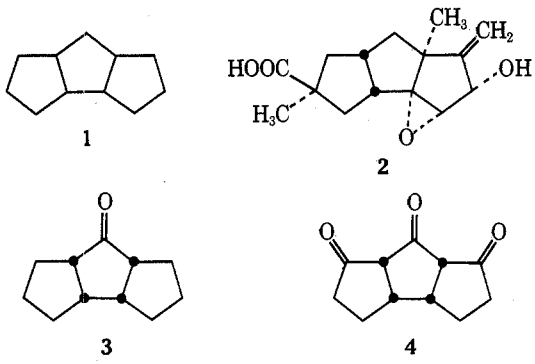
The synthesis of the first examples of compounds in the *cis,syn,cis*-tricyclo[6.3.0.$0^{3,7}$]undecane series is described. A preparatively useful synthesis of 1,1′-dicyclopentenyl ketone is given.

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

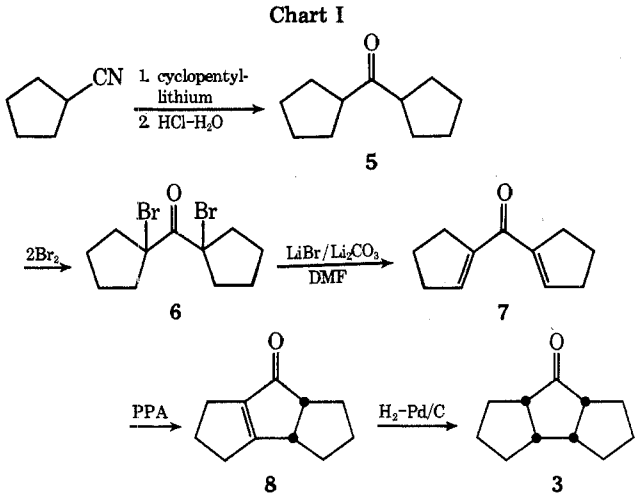
materials have appeared previously. We report now the synthesis of two simple members of the series, **3** and **4**, both particularly well suited for further elaboration.



1 **2** **3** **4**

Dicyclopentyl ketone (**5**) is available by a variety of published methods.[4] However, we found it easier to make this material by addition of commercial cyclopentyllithium to cyclopentyl nitrile, followed by hydrolysis of the imine salt. As shown in Chart I, direct bromination of dicyclopentyl ketone with 2 equiv of bromine gives **6**, which is readily dehydrobrominated with a mixture of lithium bromide and lithium carbonate in DMF. The overall yield of 1,1′-dicyclopentenyl ketone (**7**) is excellent. This method provides ready access to large quantities of this interesting cross-conjugated ketone.[5] Acid-catalyzed cyclization[6] of **7** leads into the desired tricyclic series. Acids like methanesulfonic acid or phosphorus pentoxide in methanesulfonic acid[7] give mixtures of **8** and double bond isomers. Acids with nucleophilic counterions (X^-) lead to derivatives of **3** with an X substituent α (most probably) to the carbonyl group. Fortunately, cyclization of **7** with polyphosphoric acid gives **8** cleanly and in good yield.

Chart I



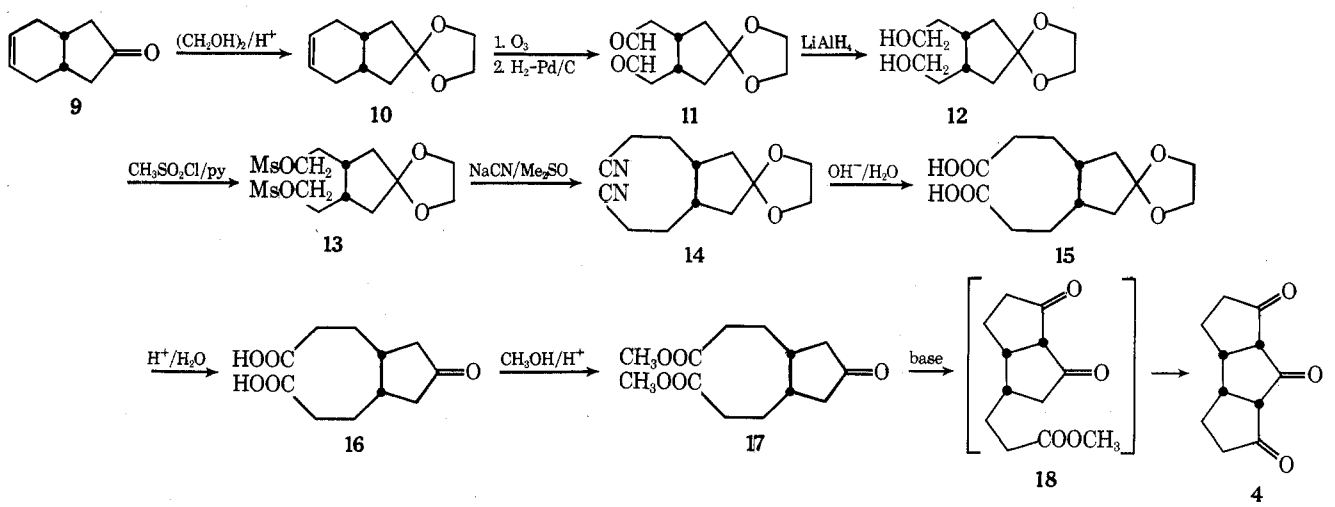
5 **6** **7** **8** **3**

The saturated ring junction in **8** is assigned cis stereochemistry. In simpler but related systems it is clear that this arrangement is much favored over the alternate trans fusion; *cis*-bicyclo[3.3.0]octan-2-one is 6 kcal/mol more stable than the trans isomer.[8] Catalytic hydrogenation of **8** over palladium on carbon gives stereospecifically *cis,syn,cis*-tricyclo[6.3.0.0^{3,7}]undecan-2-one (**3**). The assignment of this stereochemistry follows reasonably from the synthesis and, a fortiori, from ^{13}C NMR spectral data. The proton-decoupled, ^{13}C spectrum of **3** shows only six resonance lines for the 11 carbon atoms. Given the general form of the ring skeleton and assuming, quite reasonably, complete spectral resolution, this requires that **3** have C_2 or C_s symmetry; that is, both ring fusions must be cis or both must be trans. This eliminates two of the six stereochemical relationships possible in the ring system. The ^{13}C NMR spectrum of the ethylene ketal of **3** shows that the two ketal carbons see nonequivalent environments.[9] This eliminates the two isomers of C_2 symmetry, leaving only the cis,syn,cis and the trans,syn,trans possibilities. As the latter is the least favorable sterically of all the isomers, the cis,syn,cis assignment given is quite secure.

The trione **4**, functional in all three rings, can be approached in a variety of ways. We report here "the classic approach", which has the distinct advantage for the first synthesis of **4** of establishing the relative stereochemistry of the nonepimerizable centers without question. We shall present other methods in later papers. The scheme, given in Chart II, is straightforward and requires little annotation. The starting material, *cis*-bicyclo[4.3.0]non-3-en-8-one (**9**), is available easily by elaboration of *cis*-Δ^4-tetrahydrophthalic anhydride as described by Banerjee and Ram in 1972.[10] For our purposes, there was no need to purify or characterize completely any of the intermediate compounds. Indeed, we ran the synthesis using only crude intermediates and obtained, after ten steps, 6% yield overall (not optimized).

The last step in this synthesis of **4**, the base-induced cyclization of **17**, is worthy of brief comment. Many conditions were tried without success; most led only to the bicyclic ester **18**, which resists further closure. No doubt, **18** in basic media is present as its anion, the salt of a β diketone. Formation of the dianion necessary for the second cyclization is difficult. After much frustrating work, we found that potassium *tert*-butoxide

Chart II

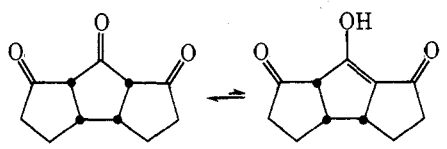


9 **10** **11** **12** **13** **14** **15** **16** **17** **18** **4**

in the aprotic, polar solvent THF is sufficiently powerful to overcome this problem without doing damage to the system.

The relative stereochemistry of the hydrogens on the tertiary carbons in **9** is not perturbed in the elaboration to **4**. The original cis configuration of adjacent centers in **9** translates to a syn relationship in the final product. The proton-decoupled ^{13}C NMR spectrum of **4** shows only six resonances for the 11 carbon atoms. These points, in combination, require that **4** be either the cis,syn,cis compound illustrated or its trans,syn,trans isomer. As we have already noted, the latter stereochemistry is very unfavorable; as such, it is most improbable for the product of the synthesis in Chart II.

Compound **4**, although a β triketone, exists predominantly in the unenolized form (eq 1). This is not unexpected. Its close



(1)

4

cousin, *cis*-bicyclo[3.3.0]octane-2,8-dione, behaves similarly.[11] Apparently, it is difficult for a three-carbon chain to bridge an sp^2 carbon to an adjacent sp^3 carbon if both are already in another five-membered ring. Still, alkali metal salts of **4** can be prepared easily.

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 run on solutions in 95% ethanol.

Standard workup refers to extraction with the stated solvent, drying with brine washes followed by treatment with sodium sulfate, and evaporation of the solvent under vacuum on a rotary evaporator.

Dicyclopentyl Ketone (5). One mole of cyclopentyllithium in cyclohexane (Foote Mineral) in 500 ml of additional cyclohexane was placed into a water-jacketed, 2-l. kettle under an atmosphere of nitrogen. Cyclopentyl nitrile[12] (90 g, 0.95 mol) in 50 ml of cyclohexane was added dropwise over 30 min. The temperature of the reaction was kept below 20 °C. The mixture turned bright yellow. It was stirred at room temperature for 1 h. Hydrolysis was then effected by adding 50 ml of 10% HCl—slowly at first, keeping the temperature below 20 °C—and then 200 ml of 30% HCl. The two-phase mixture was stirred rapidly overnight. The cyclohexane layer was separated and washed twice with 100 ml of water. The solution was dried over Na_2SO_4 and evaporated; 118 g (78%) of yellow oil was left. Distillation gave 105 g of dicyclopentyl ketone: bp 70 °C (11 mm) [lit.[4a] 113–116 °C (14 mm)]; ^1H NMR δ 2.98 (2 H, p, J = 7 Hz) and 1.3–2 ppm (16 H).

1,1′-Dibromodicyclopentyl Ketone (6). Bromine (177 g, 1.11 mol) was added dropwise to a stirred solution of dicyclopentyl ketone (92 g, 0.55 mol) in 1500 ml of carbon tetrachloride. The liberated HBr was removed by passing a stream of nitrogen over the solution. The reaction mixture was stirred at room temperature for 1 h after the addition was complete. The volatiles were removed under vacuum to leave 179 g of a yellow oil which crystallized quickly into white needles, mp 40–43 °C. This was used directly in the next step. The dibromo compound could be crystallized from CH_3OH to give material of mp 42–43 °C.

1,1′-Dicyclopentenyl Ketone (7). A uniform mixture of 80 g of lithium bromide and 80 g of lithium carbonate was added portionwise to a cold (10 °C), stirred solution of 1,1′-dibromodicyclopentyl ketone (100 g) in 700 ml of dry DMF under nitrogen. (Note well: do not add the salts separately.) The reaction mixture was warmed to 80 °C and stirred at this temperature for 4 h. The brown mixture was cooled to room temperature and poured into 1000 ml of iced water. The solution was filtered; standard workup (hexane) gave 47.4 g (95%) of yellow solid. The solid was dissolved in hexane; the solution was treated with Norit, filtered, and cooled to 0–10 °C. 1,1′-Dicyclopentenyl ketone, 35 g (70%), was obtained as pale yellow crystals: mp 61–62 °C (lit.[5] 59 °C); ir ν 1610 and 1632 cm^{-1}; uv λ 246 nm (ϵ 3950), 259 (sh, 3120), and 328 (78); ^1H NMR δ 6.56 (2 H), 1.9–2.2 (8 H), 1.32 ppm (4 H, p, $J \sim 7$ Hz).

***cis*-Tricyclo[6.3.0.0^{3,7}]undec-1(8)-en-2-one (8).** 1,1′-Dicyclopentenyl ketone (19 g) was added with good stirring to hot (100 °C) polyphosphoric acid (100 g) under nitrogen. The colorless PPA immediately turned dark brown. The reaction mixture was stirred for 30 min at 100 °C. After this time, the oil bath was replaced with an ice bath, and ice (100 g) was added immediately to the hot acid. The mixture was stirred for 5 min. A dark precipitate formed during the addition of ice, but dissolved on addition of ether. Standard workup (ether) gave a brown oil (19 g) which was distilled carefully to give the tricyclic enone **8**, better than 95% isomerically pure by GLC on OV-225, as a colorless oil (11.9 g, 62%): bp 60–63 °C (0.05 mm); ir ν 1690 and 1630 cm^{-1}; uv λ 244 nm (ϵ 3700) and 308 (72); ^1H NMR, multiplets centered at ca. δ 3.2 (1 H), 3.1 (1 H), 2.5 (2 H), 2.4 (4 H), 1.9 (1 H), 1.6 (4 H), and 1.3 ppm (1 H); 2,4-DNP, mp 201–202 °C (from $CHCl_3$/CH_3CH_2OH).

***cis,syn,cis*-Tricyclo[6.3.0.0^{3,7}]undecan-2-one (3).** Palladium on carbon (10%, 0.8 g) was added to a solution of the enone **8** (18 g) in 360 ml of ethyl acetate. The suspension was stirred at room temperature under 1 atm of H_2 until absorption was complete. The solution was filtered, and the solvent was removed under vacuum. The residue was distilled to yield 15.2 g (84%) of **3**, pure by GLC on OV-225: bp 82–84 °C (0.3 mm); ir ν 1730 cm^{-1}; ^1H NMR δ 2.9 (4 H, envelope, $W_{1/2} \sim 12$ Hz), 1.82 (2 H, m), 1.72 (4 H, m), 1.53 (4 H, p, $J \sim 7$ Hz), and 1.38 ppm (2 H, m); 2,4-DNP, mp 169–170 °C (from ethanol).

***cis,syn,cis*-Tricyclo[6.3.0.0^{3,7}]undeca-2,4,11-trione (4).** *cis*-Bicyclo[4.3.0]non-3-en-8-one (**9**, 20 g), prepared as described in the literature,[10] was combined with excess ethylene glycol (30 g) and methanesulfonic acid (1 g) in 500 ml of benzene. The mixture was stirred and heated to reflux for 24 h beneath a Dean-Stark trap. Afterwards, it was cooled and added dropwise to a well-stirred, 10% aqueous sodium carbonate solution. Standard workup (hexane) gave 23.2 g of crude, oily ketal **10**.

The majority of the crude ketal (19 g) was dissolved in 800 ml of dry ethyl acetate. The solution was cooled to about −70 °C and treated with ozone until its blue color persisted. The excess ozone was flushed out with nitrogen as the solution was warmed to 0 °C. Hydrogenation catalyst (10% Pd/C, 1.5 g) was added, and the mixture at 0–5 °C was exposed with good agitation to hydrogen at 1 atm until hydrogen absorption was complete. The catalyst was removed and the solvent evaporated in vacuo. The residue, the crude aldehyde **11**, was dissolved in 100 ml of ethyl ether, and this solution was added slowly to a suspension of lithium aluminum hydride (10 g) in a mixture of 500 ml of tetrahydrofuran and 250 ml of ether. The reaction was exothermic; the solution came to reflux. The mixture was stirred vigorously for 14 h, and then the excess hydride was destroyed with base according to the standard recipe.[13] The precipitated alumina was removed and washed with tetrahydrofuran. The organics were combined and the solvents removed in vacuo. The residue was dissolved in ether, and the solution put on a column of 200 g of silica gel. Elution with 4:1 ether/acetone gave 17 g of crude diol **12**.

The diol was dissolved in 140 ml of pyridine at 10 °C. Methanesulfonyl chloride (34 g) was added. The temperature rose to 45 °C. The solution was cooled back to 10 °C and held there for 75 min. The reaction mixture was then quenched in 500 ml of 10% aqueous sodium carbonate solution. Standard workup (methylene chloride) followed by removal of the pyridine under high vacuum gave 28 g of crude bismethanesulfonate **13**.

The crude product was dissolved in 80 ml of dry Me_2SO. This solution was added over 20 min to a well-stirred mixture under nitrogen of sodium cyanide (14 g) in 100 ml of Me_2SO at 90 °C, and the whole was maintained at this temperature for 7 h. The dark brown solution was then cooled to room temperature and poured into 600 ml of 5% aqueous sodium carbonate solution. Standard workup (ether) gave 11g of crude bisnitrile **14**.

A solution of the bisnitrile and 22 g of sodium hydroxide in 220 ml of 50% aqueous ethanol was refluxed for 7 h (→ **15** as the salt). The mixture was cooled, diluted with 200 ml of water, and extracted with methylene chloride. This extract was discarded. The aqueous phase was acidified with concentrated hydrochloric acid (→ **16**) and then taken to dryness under vacuum. The solid residue was triturated with

acetone, and the extract was evaporated under vacuum. The oily residue was taken up in 300 ml of methanol containing 0.5 ml of concentrated sulfuric acid. This solution was refluxed for 12 h, then diluted with water and extracted thoroughly with methylene chloride. The extract was concentrated under vacuum, and the residue stirred for 10 min with 50 ml of 5% hydrochloric acid. Standard workup (methylene chloride) gave 11g of crude keto ester **17**, whose quality was improved by quick passage of the material in ether through a small column of silica gel. The keto ester (10 g) showed a major ir absorption at 1740 cm^{-1}; ^1H NMR δ 3.67 (6 H), 2.2–2.4 (8 H), 1.8–2.1 (4 H), and 1.4–1.6 ppm (2 H).

A solution of **17** in 400 ml of dry tetrahydrofuran under nitrogen was mixed with 17 g of potassium *tert*-butoxide at room temperature. The suspension was stirred for 26 h. The mixture was quenched in an equal volume of saturated, aqueous potassium dihydrogen phosphate solution. Standard workup (methylene chloride) gave a solid residue which was purified by chromatography on silica gel using ether followed by 4:1 ether/acetone as eluent. Crystallization from methanol of the residue from evaporation of the ether/acetone eluate gave 1.5 g (6% overall) of pure triketone: mp 120–121 °C; ir ν 1776, 1742, and 1718 cm^{-1}; ^1H NMR δ 3.2–3.5 (4 H), 2.2–2.5 (6 H), and 1.6–1.8 ppm (2 H); ^{13}C NMR δ 208.4, 199.1 (approximate ratio 2:1), and 63.3, 40.8, 38.5, and 22.4 ppm (each of approximately equal intensity).

Acknowledgment. We are grateful to the National Institutes of Health (CA-12,961) and the National Science Foundation (GP-30568X) for financial support and to John Ivy for assistance. Funds for the purchase of the NMR instruments essential to this work were provided, in part, by the National Cancer Institute (CA-14599) via The University of Chicago Cancer Research Center, and by the National Science Foundation. C.G. thanks Montedison S.p.A., Centro Ricerche di Chimica Organica, for a leave of absence.

Registry No.—**3**, 58866-18-5; **3** 2,4-DNP, 58866-19-6; **4**, 58866-20-9; **5**, 17610-48-9; **6**, 58866-21-0; **7**, 58866-22-1; **8**, 58866-23-2; **8** 2,4-DNP, 58866-24-3; **9**, 25886-63-9; **10**, 41065-49-0; **11**, 58866-25-4; **12**, 58866-26-5; **13**, 58866-27-6; **14**, 58866-28-7; **17**, 58866-29-8; cyclopentyllithium, 23473-12-3; cyclopentylnitrile, 4254-02-8.

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Mercury in Organic Chemistry. 7.[1] A Convenient Synthesis of Symmetrical Conjugated Dienes and Polyenes

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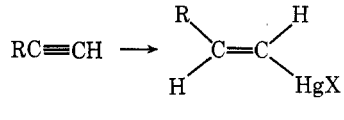
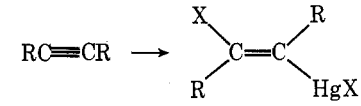
Vinylmercuric chlorides undergo reaction with palladium chloride and lithium chloride in hexamethylphosphoramide at 0 °C to provide essentially quantitative yields of the corresponding symmetrical conjugated dienes. This reaction is especially valuable for the synthesis of functionally substituted dienes and symmetrical polyenes. Divinylpalladium species are presumed to be intermediates in these reactions.

Conjugated dienes are of considerable importance in organic chemistry in themselves,[2] as well as for their utilization in the Diels–Alder reaction. Recently a number of new methods for the preparation of conjugated dienes have appeared utilizing organoaluminum,[3] -boron,[3b,4] -cobalt,[5] -copper,[6] -lithium,[5,6a-d,f,7] -magnesium,[6e] -nickel,[8] and -silver[6b,7] reagents. The scope of many of these reactions is limited by the nature of the organometallic involved or the procedure employed. Very few functional groups have been incorporated in these reactions. We wish to report a convenient new stereospecific coupling procedure utilizing vinylmercurials which both tolerates functionality and produces symmetrical dienes in near-quantitative yield. Furthermore, the reaction appears widely applicable to the preparation of symmetrical polyenes.

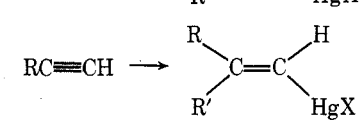
We previously reported convenient procedures for the stereospecific conversion of acetylenes into vinylmercuric halides in high yields (eq 1).[9] Other vinylmercurials are now available through the mercuration of acetylenes (eq 2, 3).[10,11]



(1)



(2)[10]



(3)[11]

Vinylmercurials possess a number of features making them attractive as synthetic intermediates. They are remarkably thermally and chemically stable organometallics. They are generally high melting, easily recrystallized solids, stable to air, water, bases, and dilute acids. These features allow one to run synthetic reactions employing these compounds under a wide variety of reaction conditions.

Recently vinylmercurials have proven valuable in the synthesis of α,β-unsaturated ketones,[12] acids,[1] and esters.[1] During the course of this latter study we observed that vinylmercuric chlorides when treated with palladium chloride and lithium chloride rapidly undergo dimerization to the