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A New Entry to the Tricyclo[6.3.0.0^{4,8}]undecane Ring System[1]

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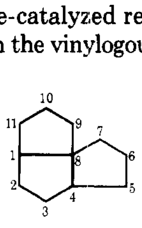
The synthesis and base-catalyzed rearrangement of vinylogous β-hydroxy ketones **3** and **36** are described. It was found that these ketones rearrange to give substituted tricyclo[6.3.0.0^{4,8}]undecanes in good yield.

A large number of terpenoids containing two or more cyclopentane rings fused in a linear fashion have been reported[2] and several of these molecules have been the target of synthetic studies.[3] Recently, a bridged spirane arrangement of three five-membered rings, i.e., the tricyclo[6.3.0.0^{4,8}]undecane ring system (**1**), was shown to be a portion of the carbon skeleton of retigeranic acid (**2**), a pentacyclic sesterterpene produced by the lichen *L. retigers*.[4] In the course of the study of the base-catalyzed rearrangement of ketol **3**, in turn prepared from the vinylogous β-diketone **4**, a new and potentially general route to the substituted tricyclo[6.3.0.0^{4,8}]undecanes[5] has been found.



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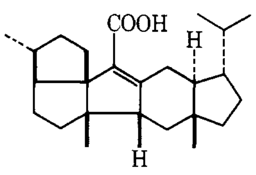

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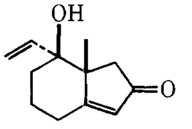

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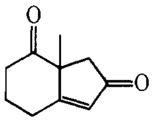

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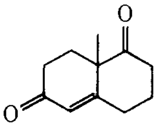
Cyclic vinylogous β-diketones, such as **5** and **6**, have been used extensively in natural product synthesis. However, a structure such as **4** in which the enone moiety resides in a *five-membered ring* has not been reported. At the outset of these studies it had been reported that upon treatment with aqueous sodium hydroxide the readily available triketone **7** underwent fragmentation followed by an aldol–dehydration reaction to afford high yields of keto acid **8**.[6] Since these conditions also failed to produce **5** from trione **9**,[7] it was decided to subject **7** to those conditions under which closure of **9** had been effected. Unfortunately, attempted closure of **7** under a variety of conditions met with uniform failure;[8] intractable tars, starting material, and **8** were the only isolable products. Therefore, it was decided to block the β-diketone moiety, the apparent source of side reactions, in attempts to convert **7** to **4**.[9] 2-Methylcyclohexane-1,3-dione was alkylated with propargyl bromide to give alkyne **10** in a 75% yield.[6] When a benzene solution of **10** was allowed to react with ethylene glycol in the presence of *p*-toluenesulfonic acid, a mixture of monoketal **11** and diketal **12** was obtained. This mixture was warmed with 50% aqueous acetic acid for a short period of time to effect hydrolysis of **12** to **11** with little hydrolysis of the monoketal. Using this procedure, crystalline monoketal was isolated in an 80% yield.[10] The triple bond was hydrated without ketal hydrolysis by stirring a solution of **11** in aqueous methanol with a catalytic amount of Dowex-50 resin impregnated with mercuric ion.[11] The resulting crude



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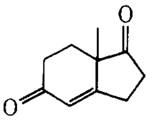

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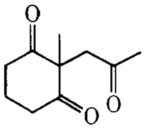

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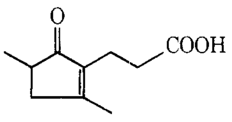

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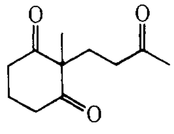

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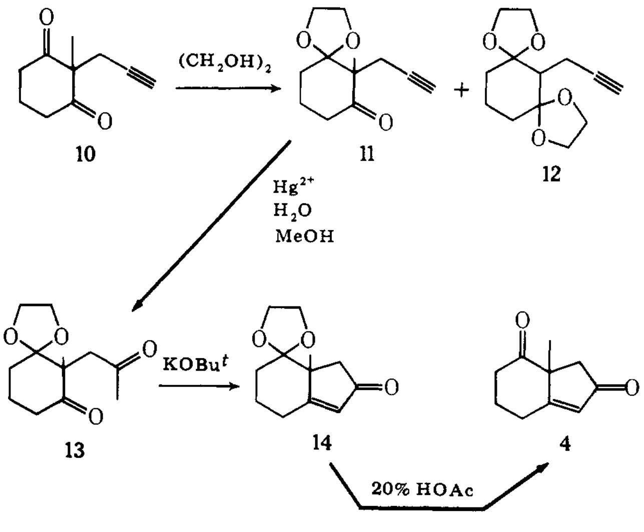
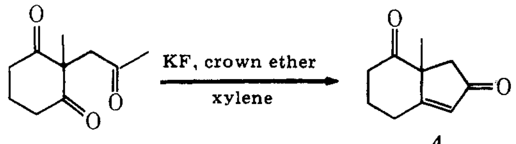


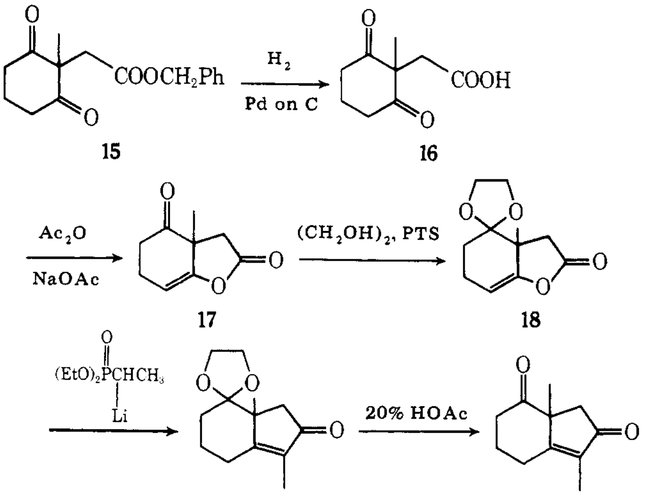
diketone **13** was treated with potassium *tert*-butoxide in *tert*-butyl alcohol to afford crystalline ketal enone **14** in a 76% overall yield from **11**. The ketal grouping of **14** was removed by allowing the material to react with warm 20% aqueous acetic acid for several hours and the desired vinylogous β-diketone **4** was obtained in 78% yield.[12]

After the completion of this work, it was discovered that when **7** was heated with potassium fluoride and dicyclohexyl-18-crown-6 in refluxing xylene a 30–40% yield of **4** was obtained. Adaptation of this method to large scale preparation of **4** was not pursued. Other studies, however, suggest that these conditions are ideal for annelation of cyclopentenone rings onto base and acid-sensitive β-diketone systems.[13]



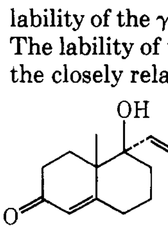
7 **4**

An alternate approach to molecules of type **4** was developed using the well-known phosphonate annelation procedure.[14] 2-Methylcyclohexane-1,3-dione was alkylated with benzyl α-bromoacetate to give a 43% yield of dione **15**, accompanied by 14% of the O-alkylation product. The benzyl group was removed by hydrogenolysis to afford a 92% yield of diketo acid **16**, which was converted to enol lactone **17** in a 75% yield upon treatment with acetic anhydride and sodium acetate. The enol lactone was converted to ketal **18** in a 75% yield using standard conditions. Ketal **18** was treated with lithium diethyl ethylphosphonate, and the resulting enone **19** was hydrolyzed to vinylogous β-diketone **20** in an overall yield of 60%.



15 **16** **17** **18** **19** **20**

One common aspect of the chemistry of diones **5** and **6** is the lability of the γ,δ bond of the vinylogous β-diketone system.[15] The lability of this bond is also observed in some reactions of the closely related vinylogous β-hydroxy ketones **21** and **22**.



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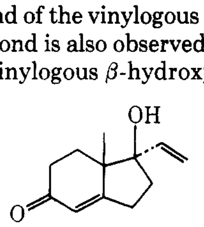

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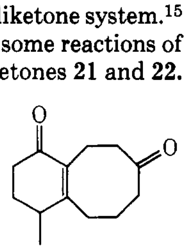

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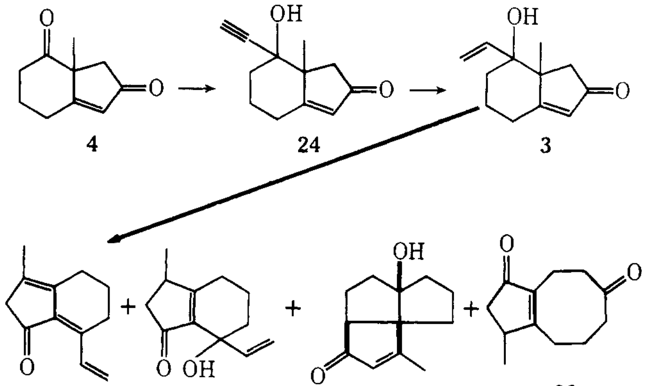
This lability was clearly demonstrated when it was shown that vinyl alcohol **21** could be converted to enedione **23** under a variety of conditions.[16] This rearrangement has been thoroughly investigated in the ring systems represented by diones **5** and **6**, but has not been investigated in systems where the enone moiety resides in a five-membered ring. Thus, attention was turned to the conversion of cyclopentenone **4** to vinyl alcohol **3**, a logical substrate for studying the effect of a cyclopentenone moiety on the aforementioned rearrangement.

When dione **4** was treated with lithium acetylide in liquid ammonia, a 78% yield of crystalline ethynyl alcohol **24** was obtained. The stereochemistry of **24** was assigned by analogy with the stereochemistry assigned to the ethynyl alcohol obtained upon treating **5** with sodium acetylide.[17] Also, according to the Felkin principle and other concepts of asymmetric induction, axial entry of the reagent should be expected in this case.[18] The synthesis of **3** was completed by hydrogenating **24** over palladium on barium sulfate in pyridine. Ketol **3** was obtained in a 79% yield after recrystallization.

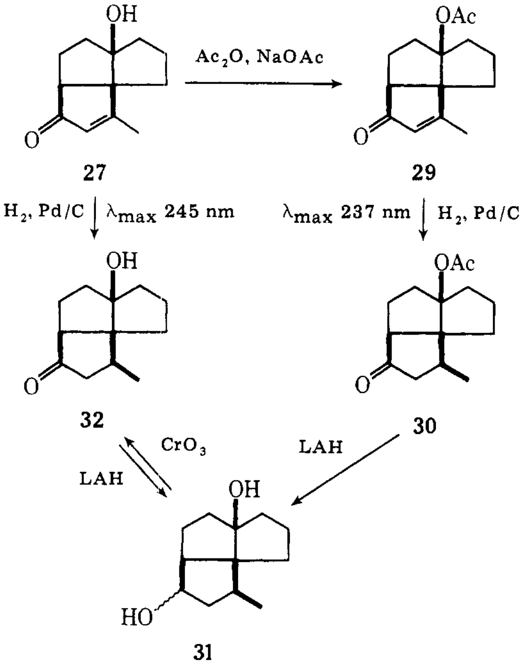


4 **24** **3**

25 **26** **27** **28**

Alcohol **3** was warmed for 9 min in refluxing 75% aqueous methanol that was 0.13 M in potassium hydroxide, and the crude product was chromatographed over silica gel. The first material that was eluted from the column was a small amount (1%) of an unstable crystalline material with a molecular weight of 178, thus showing loss of the elements of water. This material was tentatively assigned structure **25** mainly on the basis of its NMR spectrum which exhibited a methyl singlet at δ 1.80 and an ABX system typical of a conjugated vinyl group.[19] Continued elution gave a number of materials in less than 1% yield. Most of these compounds were not purified or characterized, although one substance was assigned structure **26** on the basis of spectral evidence. Finally, two products, whose mass spectra indicated that they were isomers of **3**, were isolated in yields of 8 and 48%.[20]

The major product was assigned structure **27** on the basis of the following spectral data. Absorption at 3350, 1702, and 1620 cm^{-1} in the infrared spectrum of **27** indicated the presence of a hydroxyl group, a carbonyl group, and a carbon–carbon double bond. The ^{1}H NMR spectrum exhibited a single vinyl proton at δ 5.83 which was allylically coupled to a methyl group at δ 2.18. These signals are typical of β-methyl enones.[21] Furthermore, an absence of signals in the δ 3.5–4.5 region of the spectrum indicated that the alcohol was tertiary. The proton noise- and off-resonance-decoupled ^{13}C NMR spectra of **27** (Table I) provided additional support for the assigned structure. The proton noise-decoupled spectrum exhibited 12 signals. Four of these signals remained singlets in the off-resonance-decoupled spectrum, confirming the presence of four quaternary carbon atoms. The chemical shifts and multiplicities of the remaining signals were consistent with the assigned structure. The ultraviolet spectrum of **27** showed a maximum at 245 nm (ϵ 7800) in methanol. Although this value is not in accord with the maxium of 226 nm predicted by Woodward's rules,[22] it can be explained by the present of a σ-coupled π-electron system.[23] For such an effect, it has been shown that isolated p-electron systems, when appropriately linked by overlap through a σ bond, can constitute unique chromophores.[24] Overlap between the enone π electrons and an oxygen lone pair via the C-1,8 σ bond is possible in **27**. Thus, this chromophore may absorb light in a completely different fashion than an unperturbed cyclopentenone. Alternatively, the bathochromic shift observed in **27** relative to other cyclopentenones may be due to the proximity of the polar hydroxyl group to the chromophore. It is well known that polar solvents caused bathochromic shifts in the $\pi-\pi^*$ excitation of enones.[25] The additional presence of internal polarity in the form of the rigidly held hydroxyl group may be responsible for the bathochromic shift observed in **27**. In agreement with this interpretation of the ultraviolet spectrum, acetate **29** exhibited a $\pi-\pi^*$ maximum at 237 nm in methanol. It should be noted that the cis–cis stereochemistry, originally assigned to **27** on the basis on the thermodynamic stabilities of *cis*- and *trans*-bicyclo[3.3.0]octanes,[26] is supported by the observed "abnormal" ultraviolet spectrum.



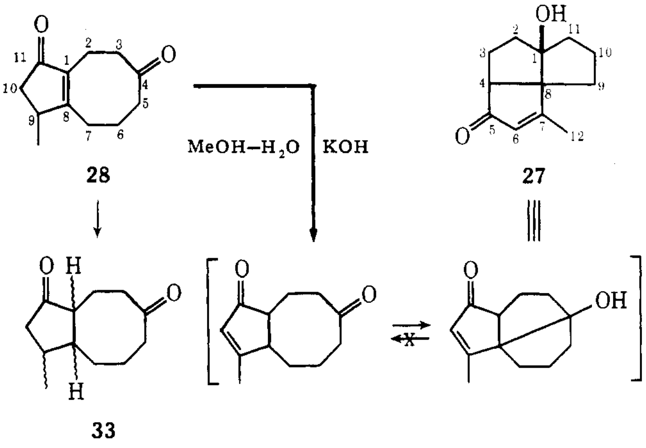
The following reactions also support the assignment of structure **27** to the major rearrangement product. Ketol **27** was converted to crystalline acetate **29** upon treatment with acetic anhydride and sodium acetate. Catalytic reduction of **29** gave acetate **30**. This acetate was resistant to mild base hydrolysis, but was converted to ketol **32** upon treatment with lithium aluminum hydride and subsequent Jones oxidation of the resulting diol **31**. Ketol **32**, derived by this route, was identical to material prepared by direct hydrogenation of **27**. Absorption at 1741 cm^{-1} in the infrared spectrum of **32** demonstrated the presence of a cyclopentanone moiety. As expected, ketol **32** exchanged only three carbon-bound protons upon treatment with MeONa-MeOD. The C-7 methyl groups in molecules **30–32** were assigned endo stereochemistry due to expected hydrogenation from the convex face of the bicyclo[3.3.0]octane system.

The minor rearrangement product was assigned structure **28** on the basis of the following evidence. The proton NMR spectrum of **28** exhibited a three-proton multiplet at δ 1.17 and showed no signals below δ 2.80. Infrared absorption of 1705 and 1616 cm^{-1} indicated the presence of at least once carbonyl group and a carbon–carbon double bond. The ultraviolet spectrum of **28** showed a maximum at 240 nm in methanol, consistent with an α,β-dialkylcyclopentenone. Catalytic hydrogenation of **28** produced a mixture of dihydro isomers **33** whose infrared spectrum showed carbonyl absorption at 1750 and 1705 cm^{-1}, confirming the presence of five- and eight-membered ring ketones. Upon reaction with potassium hydroxide in 75% aqueous methanol, **28** was slowly converted to ketol **27**, illustrating the structural relationship between the two isomers. When **28** was rearranged to **27** in MeONa–MeOD, the ^{13}C NMR spectrum of the resulting deuterated **27** revealed that deuterium had been incorporated on the carbons resonating at 131.5, 59.9, 41.4, 39.1, 35.4, and 17.4 ppm.[27] When **27** was treated with MeOD–MeONa, only the carbons resonating at 131.5, 59.9, and 17.4 ppm incorporated deuterium. Thus, three carbon atoms in **28** bear exchangeable protons that become nonexchangeable in **27**. These three carbon atoms are undoubtedly carbons 3, 5, and 7 in **28** which become carbons 2, 11, and 9 in **27**, respectively. These exchange data firmly support the assigned structures. Also, the fact that no deuterium could be incorporated at carbon atoms 2, 9, and 11 upon treating **27** with MeOD–MeONa indicates that the ring closure itself is irreversible under the conditions examined here.

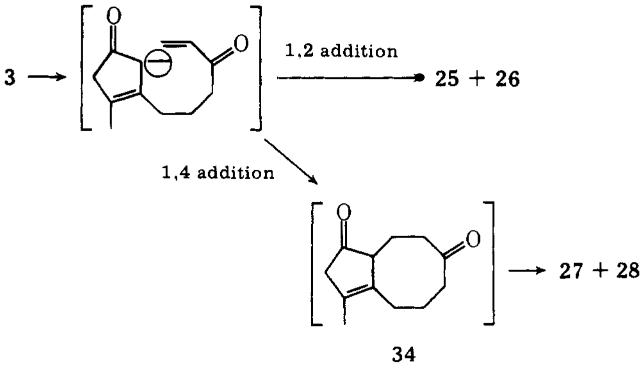
Table I. ^{13}C NMR Spectra of Ketol 27

Chemical shift[a]	Multiplicity[b]	Assignment[c]	Chemical shift[a]	Multiplicity[b]	Assignment[c]
191.7	s	C-5	41.4	t	C-2, 9, 11
182.7	s	C-7	39.1	t	C-2, 9, 11
131.5	d	C-6	35.4	t	C-2, 9, 11
91.1	s	C-1	25.4	t	C-3, 10
66.1	s	C-8	24.5	t	C-3, 10
59.9	d	C-4	17.4	q	C-12

[a] ppm from internal Me$_4$Si. [b] Taken from the off-resonance-decoupled spectrum [c] The partial assignment of the methylene carbons is briefly discussed in the text.

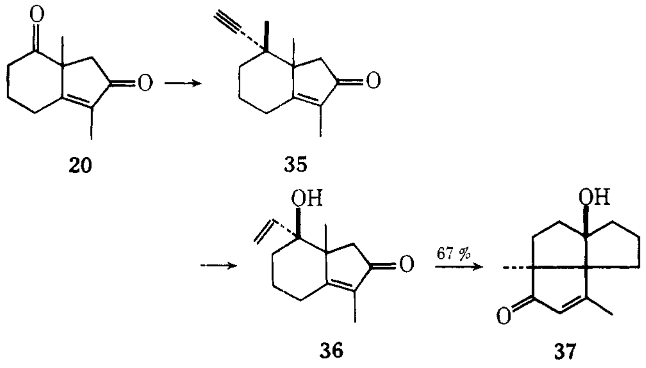


As in the analogous rearrangement of ketol **21**, the observed products from the rearrangement of **3** can be accounted for by a vinylogous retro-aldol condensation followed by intramolecular 1,2 and 1,4 addition of an intermediate dienolate to the resulting enone moiety. When 1,4 addition occurs, conjugation of the double bond in the presumed intermediate **34** toward the ring juncture gives **28**. Conjugation away from the ring juncture followed by a transannular vinylogous aldol condensation produces **27**.[28,29] This result is a direct consequence of the presence of a cyclopentenone moiety in the rearrangement system. Since dione **28** was found to rearrange



to **27** much more slowly than either **27** or **28** were formed during the rearrangement of **3**, the ratio of **27** to **28** formed during the rearrangement reflects the kinetic partitioning of the presumed intermediate **34** between the two isomeric products.

The potential generality of this route to tricyclo[6.3.0.0^{4,8}]-undecanes was underscored by the rearrangement of vinyl alcohol **36**, prepared in 42% yield from dione **20** via ethynyl alcohol **35**, to the crystalline ketol **37**. This ketol contains the angular methyl group present in the tricyclo[6.3.0.0^{4,8}]undecane moiety of retigeranic acid. Thus, the now readily available hydrindenes of type **4** appear to be valuable intermediates in the synthesis of substituted tricyclo[6.3.0.0^{4,8}]undecanes.



20 **35** **36** **37**

Experimental Section

General. All melting points were determined on a Mel-Temp Laboratory Device and are uncorrected, as are boiling points. Proton magnetic resonance spectra (60 MHz) were recorded on Varian T-60 or Perkin-Elmer R-24A instruments. Chemical shifts are reported in units of δ from internal tetramethylsilane. Carbon-13 magnetic resonance spectra (25 MHz) were recorded on a NTC-TT-23 spectrometer (Nicolet) and are reported in ppm from internal tetramethylsilane. Infrared spectra were taken on Perkin-Elmer 137, 237, or 710A spectrometers and ultraviolet spectra on a Perkin-Elmer Model 202 instrument. Mass spectral data were collected on AEI-MS-12 and CEC-21-110B instruments. Combustion analyses were carried out by the University of California Microanalytical Laboratory.

Solvents were dried and distilled prior to use when deemed necessary: diethyl ether and tetrahydrofuran (from Na metal), ammonia (from Li or Na metal), *N,N*-dimethylformamide (from calcium hydride), methanol and ethanol (from magnesium methoxide and magnesium ethoxide, respectively).

Analytical and preparative vapor-phase chromatography were carried out predominantly on Hewlett-Packard 402 and Varian Aerograph A-90-P machines, respectively. Dry nitrogen was used in reactions requiring an inert atmosphere. Most reactions were followed by thin-layer chromatography over silica gel, vapor-phase chromatography, or ^{1}H NMR spectroscopy. Bulb to bulb distillations were performed in a Büchi Kugelrohrapperat.

2-Methyl-2-(prop-2-yn-1-yl)cyclohexane-1,3-dione (10).[6] Dione **10** was prepared according to a modification of an established procedure.[6] To a stirred suspension of 21.6 g (0.90 mol) of sodium hydride in 550 mL of *N,N*-dimethylformamide was added 113.4 g (0.90 mol) of 2-methylcyclohexane-1,3-dione[30] in small portions over a 20-min period. To the resulting solution was added 119.0 g (1.0 mol) of propargyl bromide over a 30-min period. The mixture was stirred overnight at room temperature and poured into 2 L of methylene chloride–water (1:1). The organic phase was washed with water (four 1-L portions), dried ($MgSO_4$), and concentrated at reduced pressure. The residual liquid was distilled to afford 110.0 g (73%) of dione **10**, bp 95–100 °C at 1.0 mm, whose spectra agreed with those reported elsewhere.[6]

2-Acetonyl-2-methylcyclohexane-1,3-dione (7).[6] Trione **7** was prepared according to a modification of an established procedure.[6] To a stirred solution of 450 mg (2.64 mmol) of alkyne **10** in 9 mL of methanol–water (2:1) was added 50 mg of Dowex-50 ion-exchange resin impregnated with mercuric ion[11] and one drop of concentrated H_2SO_4. The mixture was stirred for 24 h at room temperature and poured into 10 mL of water. The resulting solution was extracted with ether (two 25-mL portions). The extracts were dried ($MgSO_4$) and concentrated to afford 357 mg (71%) of crystalline trione **7**, mp 60–64 °C (lit.[6] 65–66 °C). This material exhibited spectral data in agreement with those previously reported for **7**.

6-Methyl-6-(prop-2-yn-1-yl)-1,4-dioxaspiro[4.5]decan-7-one (11). A vigorously stirred mixture of 110.0 g (0.65 mol) of alkyne **10**, 150 mL of ethylene glycol, 100 mg of *p*-toluenesulfonic acid, and 900 mL of benzene was heated under reflux for 17 h with azeotropic removal of 17 mL of water. The solution was cooled, washed with 500 mL of water, dried ($MgSO_4$), and concentrated. The solid residue was recrystallized from 150 mL of CCl_4 to give 88.5 g (59%) of monoketal **11**: mp 120–122 °C; IR ($CHCl_3$) 3250, 1710 cm^{-1}; NMR (CCl_4) δ 1.20 (s, 3), 1.56–1.89 (m, 5), 2.19–2.61 (m, 4), 3.93 (s, 4); MS (70 eV) *m/e* 208 (M$^+$), 193, 99 (base).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.95; H, 7.72.

The mother liquor was shown by VPC (10 ft × 0.25 in. 5% SE-30, 200 °C) to be mainly diketal **12** along with some dione **10** and monoketal **11**. To this mixture was added 150 mL of 50% aqueous acetic acid. The solution was warmed for 10 min on a steam bath followed by cooling in an ice bath. The resulting crystals were collected and recrystallized from carbon tetrachloride to give an additional 20.0 g (15%) of **11**. A purified sample of diketal **12** exhibited the following properties: mp 107–109 °C; NMR (CCl_4) δ 1.28 (s, 3), 1.40–1.80 (m, 7), 2.37 (d, 2, J = 2.5 Hz), 3.90 (m, 8); MS (70 eV) *m/e* 252 (M$^+$), 99 (base).

Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.53; H, 7.85.

7,7-(Ethylenedioxy)-7a-methyl-2,4,5,6,7,7a-hexahyrdroinden-2-one (14). To a solution of 78.5 g (0.377 mol) of ketal **11** in 2-L of methanol-water (4:1) was added 140 mg of mercurated Dowex-50 ion-exchange resin[11] and one drop of concentrated H_2SO_4. The mixture was stirred for 24 h at room temperature and an additional 1.0 g of resin was added. The mixture was allowed to stir for an additional 24 h and was poured into 2 L of water. The resulting mixture was extracted with methylene chloride (one 2-L and one 1-L portions) and the combined extracts were washed with 2 L of water. The organic solution was dried (Na_2SO_4) and concentrated to afford 80 g of crude dione **13** as a colorless liquid, homogeneous by TLC (silica gel; ethyl acetate–benzene, 3:7) and exhibiting the following spectral properties: IR (CCl_4) 1730 cm^{-1}; NMR (CCl_v) δ 1.32 (s, 3), 1.60–2.10 (m, 4), 2.10 (m, 4), 2.10 (s, 3), 2.10–2.70 (m, 4), 3.86 (s, 4); MS (70 eV) *m/e* 226 (M$^+$).

To a solution of 41.6 g (0.37 mol) of potassium *tert*-butoxide in 1.6 L of *tert*-butyl alcohol was added the crude **13** in 200 mL of *tert*-butyl alcohol over a 2-h period. The mixture was stirred for an additional 30 min, poured into 2-L of ice-cold 10% HCl and extracted with 2 L of methylene chloride. The extract was washed with water (four 2-L portions), dried (Na_2SO_4), and concentrated. The semicrystalline residue was recrystallized from 1.6 L of petroleum ether (30–60 °C) to give 61.0 g (78%) of enone **14**: mp 86–88 °C; UV λ_{max} (MeOH) 235 nm (ϵ 7800); IR (CCl_4) 1705, 1630 cm^{-1}; NMR (CCl_4) δ 1.37 (s, 3), 1.50–2.05 (m, 6), 2.25–2.77 (m, 2), 3.95 (s, 4), 5.69 (s, 1); MS (70 eV) *m/e* 208 (M$^+$), 99 (base).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.88; H, 7.51.

7a-Methyl-2,4,5,6,7,7a-hexahydroindene-2,7-dione (4). (A) From Ketal 14. A solution of 75.6 g (0.362 mol) of ketal **14** in 700 mL of 20% aqueous acetic acid was stirred at 95 °C for 7 h. The mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with chloroform. The extract was dried ($MgSO_4$) and concentrated at reduced pressure. The residue was recrystallized from hexane–benzene to give 19.8 g of dione **4**. The mother liquor was filtered through silica gel with benzene as eluant and the eluted material was recrystallized to give an additional 18.0 g (70%) of **4**: mp 74–77 °C; UV λ_{max} (MeOH) 241 nm (ϵ 4700); IR (CCl_4) 1710, 1625 cm^{-1}; NMR (CCl_4) δ 1.50 (s, 3), 1.7–3.18 (m, 8), 5.50 (br s, 1); MS (70 eV) *m/e* 164 (M$^+$).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.99; H, 7.20.

(B) From Trione 7. A mixture of 182 mg (1.0 mmol) of trione **7**, 96 mg (2.0 mmol) of anhydrous potassium fluoride, and 74 mg (0.2 mmol) of dibenzo-18-crown-6[31] in 7 mL of *p*-xylene was heated under reflux for 20 h with continuous removal of water using a Dean-Stark trap filled with Linde 4A molecular sieves. The solvent was removed at reduced pressure, and the residue was chromatographed over silica gel to afford 75 mg of crude dione **4**. This material was recrystallized from benzene–hexane to give 50 mg (3) of pure **4**, identical in all respects to a sample prepared by the method described above.

Benzyl α-(1-Methyl-2,6-dioxocyclohexyl)acetate (15). To a suspension of 3.59 g (0.15 mol) of sodium hydride in 125 mL of *N,N*-dimethylformamide was added 18.9 g (0.15 mol) of 2-methylcylohexane-1,3-dione[30] in small portions over a 15-min period. To the resulting solution was added 34.2 g (0.15 mol) of benzyl α-bromoacetate[32] over a 60-min period. The mixture was stirred at room temperature for 20 h followed by the addition of 500 mL of ether. The solution was washed with water (four 500-mL portions), dried ($MgSO_4$), and concentrated. The residual solid was recrystallized from ether–hexane (1:1) to give 15.5 g (38%) of diketo ester **15:** mp 88–89 °C; IR (CCl_4) 1730, 1705 cm^{-1}; NMR (CCl_4) δ 1.18 (s, 3), 2.0 (m, 2), 2.55 (m, 4), 2.95 (s, 2), 4.95 (s, 2), 7.16 (s, 5); MS (70 eV) *m/e* 274 (M^+), 92 (base).

Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.93; H, 6.60.

The mother liquor was a mixture of **15** and the O-alkylation product. These could be separated by chromatography over silica gel (benzene–ethyl acetate, 9:1) to afford additional **15.**

α-(1-Methyl-2,6-dioxocyclohexyl)acetic Acid (16). A solution of 15.5 g (56.5 mmol) of ester **15** in 180 mL of ethanol–ethyl acetate (7:2) was hydrogenated over palladium on charcoal at 1 atm and room temperature until hydrogen uptake ceased (90 min). The solution was filtered through Celite and concentrated, and the residual solid was recrystallized from benzene to give 9.5 g (92%) of diketo acid **16:** mp 175–178 °C; NMR ($CDCl_3$) δ 1.28 (s, 3), 2.10 (m, 2), 2.62 (m, 4), 3.08 (s, 2), 9.2 (br s, 1); MS (70 eV) *m/e* 184 (M^+), 69 (base).

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.52. Found: C, 58.47; H, 6.30.

1-Methyl-7-oxabicyclo[4.3.0]non-5-ene-2,8-dione (17). A solution of 9.2 g (52.0 mmol) of acid **16** in 60 mL of acetic anhydride was heated under reflux for 75 min followed by the addition of 200 mg of anhydrous sodium acetate. The mixture was heated for an additional 150 min followed by removal of the acetic anhydride at reduced pressure and ambient temperature. The residual oil was chromatographed over silica gel (eluted with benzene–ethyl acetate, 9:1). The crude eluate was distilled to afford 6.0 g (69.6%) of enol lactone **17:** bp 125–130 °C (1.0 mm); IR (CCl_4) 1825, 1720, 1700, 1205, 1075 cm^{-1}; NMR (CCl_4) δ 1.44 (s, 3), 2.42 (br m, 6), 5.33 (m, 1); MS (70 eV) *m/e* 166 (M^+), 151, 138, 124, 96, 69, 55 (base).

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.10; H, 6.02.

2,2-Ethylenedioxy-1-methyl-7-oxabicyclo[4.3.0]non-5-en-8-one (18). A mixture of 6.0 g (36.1 mmol) of enol lactone **17,** 8.0 mL of ethylene glycol, and 15 mg of *p*-toluenesulfonic acid in 70 mL of benzene was heated under reflux with azeotropic removal of water for 4 h. The solution was cooled, washed thoroughly with water, dried (Na_2SO_4), and concentrated to give a yellow oil which crystallized upon standing. This material was recrystallized from hexane–carbon tetrachloride to yield 3.02 g of ketal **18** as white needles, mp 84–86 °C. The mother liquor was chromatographed over silica gel (eluted with ether) to give an additional 1.5 g (60%) of **18:** IR (CCl_4) 1818, 1709 cm^{-1}; NMR (CCl_4) δ 1.33 (s, 3), 1.6–2.5 (m, 5), 2.80 (d, 1, J = 16 Hz), 3.87 (s, 4), 4.98 (t, 1, J = 3 Hz); MS (70 eV) *m/e* 210 (M^+), 86 (base).

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.70; H, 6.85.

3,7a-Dimethyl-2,4,5,6,6,6a-hexahydroindene-2,7-dione (20). To a solution of 1.33 g (8.0 mmol) of diethyl ethylphosphonate in 20 mL of tetrahydrofuran at −50 °C was added 2.7 mL (6.0 mmol) of 2.2 M *n*-butyllithium in hexane. The mixture was stirred under nitrogen for 20 min followed by dropwise addition of a solution of 420 mg (2.0 mmol) of ketal **18** in 5 mL of tetrahydrofuran over a 30-min period. The resulting yellow solution was stirred at −55 °C for 75 min followed by the addition of 108 mg (2.0 mmol) of sodium methoxide in 10 mL of methanol. The solution was stirred at room temperature for 21 h, heated under reflux for an additional 3 h, and concentrated at reduced pressure. The residue was partitioned between 50 mL of ether and 50 mL of water. The aqueous layer was extracted with 50 mL of ether and the combined organic layers were dried and concentrated. The residual oil was chromatographed over 10 g of silica gel (eluted with ether) to give 275 mg (62%) of enone **19** as a colorless liquid, suitable for use in subsequent reactions: UV λ_{max} (MeOH) 243 nm (ϵ 10 000); IR (CCl_4) 1700, 1655 cm^{-1}; NMR (CCl_4) δ 1.30 (s, 3), 1.5–2.7 (m, 11, with br s at 1.60 and d's, J = 18 Hz, at 1.69 and 2.42), 3.90 (s, 4); MS (70 eV) *m/e* 222 (M^+), 99 (base).

A solution of 265 mg (1.19 mmol) of enone **19** in 5 mL of acetic acid–water (1:4) was warmed at 90 °C for 200 min. The resulting yellow solution was cast into an excess of saturated aqueous $NaHCO_3$, extracted with dichloromethane and concentrated. The residual oil was chromatographed over 10 g of silica gel (eluted with ether) to give 196 mg (92%) of dione **20:** IR (CCl_4) 171 (br), 1658 cm^{-1}; NMR (CCl_4) δ 1.47 (s, 3), 1.62 (s, 3), 1.7–3.1 (m, 8); MS (70 eV) *m/e* 178 (M^+), 79 (base).

Exact mass calcd for $C_{11}H_{14}O_2$: 178.0993. Found: 178.0975.

7α-Ethynyl-7β-hydroxy-7aβ-methyl-2,4,5,6,7,7a-hexahydroinden-2-one (24). To a solution of 750 mL of ammonia at −78 °C through which acetylene was rapidly bubbled was added 1.64 g (0.24 mol) of lithium metal. To the resulting colorless solution was added a solution of 19.2 g (0.117 mol) of dione **4** in 500 mL of ether over a 20-min period. The solution was stirred under nitrogen for an additional 20 min followed by the addition of 10.8 g (0.24 mol) of ammonium chloride in 700 mL of water. The ammonia was allowed to evaporate followed by the addition of 1 L of water. The ether layer was separated and the aqueous layer was extracted with methylene chloride (two 750-mL portions). The combined extracts were dried ($MgSO_4$) and concentrated. The residual solid was recrystallized from 110 mL of CCl_4–EtOAc (1:1) to give 16.8 g (76%) of ethynyl alcohol **24:** mp 161–162 °C; UV λ_{max} (MeOH) 239 nm (ϵ 6200); IR ($CDCl_3$) 3600, 3300, 1705, 1620 cm^{-1}; NMR ($CDCl_3$) δ 1.31 (s, 3), 1.85–3.21 (m, 10), 5.85 (s, 1); MS (70 eV) *m/e* 190 (M^+).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.54; H, 7.31.

7β-Hydroxy-7aβ-methyl-7α-vinyl-2,4,5,6,7,7a-hexahydroinden-2-one (3). A mixture of 16.0 g (0.084 mol) of ethynyl alcohol **24** and 3.1 g of 5% Pd on $BaSO_4$ in 160 mL of pyridine was hydrogenated at 1 atm and room temperature until 1 equiv of hydrogen had been consumed. The solution was poured into 500 mL of methylene chloride, filtered through Celite, washed with 10% aqueous hydrochloric acid (two 1-L portions), dried (Na_2SO_4) and concentrated at reduced pressure. The resdual solid was recrystallized from CCl_4–hexane (2:1) to afford 11.2 g (70%) of vinyl alcohol **3:** mp 94–96 °C; UV λ_{max} (MeOH) 241 nm (ϵ 7200); IR ($CHCl_3$) 3300, 1703, 1675, 1630 cm^{-1}; NMR (CCl_4) δ 1.38 (s, 3), 1.51–2.68 (m, 9), 4.98–6.27 (m, 4); MS (70 eV) *m/e* 192 (M^+), 122 (base).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.78; H, 8.26.

Base-Catalyzed Rearrangement of Vinyl Alcohol 3. A solution of 5.0 g (26.0 mmol) of vinyl alcohol **3** and 0.75 g of potassium hydroxide in 100 mL of methanol–water (3:1) was heated under reflux for a 9-min period. The dark solution was poured into 300 mL of ether–water (2:1). The organic layer was separated and the aqueous layer was extracted with 100 mL of ether. The combined organic layers were dried ($MgSO_4$) and concentrated to yield 4.1 g of an orange oil. This material was chromatographed over 250 g of silica gel (eluted with benzene–ethyl acetate, 85:15) with the collection of approximately 100 mL fractions. Fractions 5–8 afforded 50 mg (1%) of an unstable crystalline substance, tentatively assigned the structure of trienone **25:** mp 63–70 °C; IR (CCl_4) 1707, 1634, 1599, 1571, 909 cm^{-1}; NMR (CCl_4) δ 1.8 (m, 5, with s at 1.80), 2.4 (m, 4), 2.8 (m, 2), 5.2 (d, 1, J = 11 Hz), 5.45 (d, 1, J = 16 Hz), 7.8 (dd, 1, J = 11 Hz, 16); MS (70 eV) *m/e* 174 (M^+), 159, 147, 146, 131, 43.

Fractions 15–18 afforded 40 mg of a complex mixture of products. Fractions 19–22 contained two components by high-pressure liquid chromatography (4 ft × ⅛ in. Corasil II; hexane–chloroform, 2:1; 2.5 mL min^{-1}), one of which was isolated and tentatively assigned structure **26** on the basis of spectral data: UV λ_{max} (MeOH) 235 nm (ϵ 5500); IR (CCl_4) 3350, 1700 (sh), 1690, 1658 cm^{-1}; NMR (CCl_4) δ 1.22 (d, 3, J = 6 Hz), 1.5–2.9 (m, 9), 3.5 (br s, 1), 4.87 (dd, 1, J = 16 Hz, 1), 5.04 (dd, 1, J = 10 Hz, 1), 5.92 (dd, 1, J = 16 Hz, 10); MS (70 eV) *m/e* 192 (M^+).

Fractions 23–30 afforded 400 mg of a mixture of products including some **26.** Fractions 31–41 gave 400 mg (8%) of dione **28** as a homogeneous oil (VPC, TLC): UV λ_{max} (MeOH) 240 nm (ϵ 7200); IR (CCl_4) 1705, 1616 cm^{-1}; NMR (CCl_4) δ 1.17 (d, 3, J = 6 Hz), 1.6–2.8 (m, 13); MS (60 eV) *m/e* 192 (M^+), 136 (base).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.70; H, 8.35.

Fractions 45–90 gave 2.4 g (48%) of ketol **27** as a homogeneous oil (VPC, TLC): UV λ_{max} (MeOH) 245 nm (ϵ 7800); UV λ_{max} (hexane) δ 241 nm (ϵ 7800); IR (CCl_4) 3350, 1702, 1620 cm^{-1}; NMR (CCl_4) δ 1.6–2.4 [m, 15, with d, J = 1 Hz, at 2.18 and s (−OH) at 2.40], 5.83 (q, 1, J = 1 Hz); MS (70 eV) *m/e* 192 (M^+).

Exact mass calcd for $C_{12}H_{16}O_2$: 192.1150. Found: 192.1149.

1-Acetoxy-7-methyltricyclo[6.3.0.$0^{4,8}$]undec-6-en-5-one (29). A mixture of 102 mg (1.0 mmol) of ketol **27** and 164 mg (2.0 mmol) of anhydrous sodium acetate in 2.6 mL of acetic anhydride was stirred under nitrogen at 85 °C for 28 h. The solution was poured into saturated aqueous sodium bicarbonate and the resulting mixture was extracted with dichloromethane. The extract was dried (Na_2SO_4) and concentrated. The residual oil was bulb to bulb distilled to give 199 mg (84%) of acetate **29:** bp 145 °C (0.05 mm); UV λ_{max} (MeOH) 237 nm (ϵ 10 900); IR (CCl_4) 1730, 1705 cm^{-1}; NMR (CCl_4) δ 1.4–2.7 (m, 17, with s at 2.10 and d, J = 1 Hz, at 2.2), 5.84 (q, 1, J = 1 Hz); MS (70 eV) *m/e* 234 (M^+), 164, 43 (base).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.66; H, 7.74.

1-Acetoxy-7-methyltricyclo[6.3.0.0^{4,8}]undecan-5-one (30). A solution of 199 mg (0.84 mmol) of enone **29** in 10 mL of absolute ethanol was hydrogenated at room temperature and 1 atm over 90 mg of 5% palladium on charcoal until uptake of hydrogen ceased (20 mL). The solution was filtered and concentrated. The residue was sublimed at 60 °C and 0.2 mm to afford 160 mg (80%) of ketone **30** as a waxy solid: mp 44–48 °C; IR (CCl_4) 1735 cm^{-1} (br); NMR (CCl_4) δ 1.30 (m, 3), 1.6–2.6 (m, 17, with s at 1.90); MS (70 eV) *m/e* 236 (M$^+$), 43 (base).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.23; H, 8.21.

7-Methyltricyclo[6.3.0.0^{4,8}]undecan-5-on-1-ol (32). (A) From Ketone 30. To a solution of 85 mg (0.36 mmol) of ketoacetate **30** in 10 mL of ether was added an excess of solid lithium aluminum hydride. The mixture was stirred at room temperature for 60 min, quenched with water, filtered, and concentrated to give 70 mg of crude diol **31** which was used directly in the next reaction: mp 118–127 °C; IR ($CDCl_3$) 3600, 3350 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (m, 3), 1.6–2.4 (m, 16), 4.07 (m, 1); MS (70 eV) *m/e* 196 (M$^+$), 178, 163, 160, 145, 79 (base).

To the crude diol **31** in 5 mL of acetone at 0 °C was added an excess of Jones reagent. The mixture was stirred for a few minutes and cast into a mixture of water and methylene chloride. The organic layer was washed with saturated aqueous sodium bicarbonate, dried (Na_2SO_4), and concentrated to give 61 mg (87%) of **32**, at least 90% pure by VPC (10 ft × 1/4 in. 5% SE-30, 205 °C). An analytically pure sample of this waxy solid was prepared by preparative VPC: mp 109–113 °C; IR (CCl_4) 3600, 3350, 1741 cm^{-1}; NMR ($CDCl_3$) 1.33 (m, 3), 1.5–2.6 (m, 15); MS (70 eV) *m/e* 194 (M$^+$).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.40; H, 9.07.

(B) From Ketol 27. A solution of 188 mg (0.98 mmol) of **27** in 5 mL of absolute ethanol was hydrogenated over 57 mg of 5% palladium on charcoal at 1 atm and room temperature. The solution was filtered through Celite and concentrated to afford 188 mg (99%) of crude **32**. A sample whose melting point and spectral properties were identical to those of ketol **32** prepared by method A was prepared by preparative VPC. A mixture of ketols **32** prepared by methods A and B melted undepressed, mp 109–112 °C.

Ketol **32** exchanged three protons upon treatment with MeOD–MeONa. The three-proton signal at δ 1.33 in **32**-d_3 appeared as a doublet, J = 6 Hz. Ketol **32**-d_3 was reduced with lithium aluminum hydride to give **31**-d_3: mp 125–126 °C (recrystallized from CCl_4); NMR (CCl_4) δ 1.23 (d, 3, J = 6 Hz); MS (70 eV) *m/e* 199 (M$^+$). When ketol **27** was sequentially hydrogenated and treated with LAH, a 70% yield of **31** was obtained.

9-Methylbicyclo[6.3.0]undecane-4,11-dione (33). A solution of 55 mg (0.29 mmol) of enedione **28** in 8 mL of absolute ethanol was hydrogenated over 27 mg of 10% palladium on charcoal at 1 atm and room temperature. The solution was filtered and concentrated to afford 54 mg of crude dione **33**. An analytically pure sample of **33** was prepared by preparative VPC (10 ft × 1/4 in. 5% SE-30, 190 °C): IR (CCl_4) 1750, 1705 cm^{-1}; NMR (CCl_4) δ 1.15 (m, 3), 1.15–2.6 (m, 15); MS (70 eV) *m/e* 194 (M$^+$), 179, 151 (base).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: 73.96; H, 9.18.

Base-Catalyzed Rearrangement of Dione 28. (A) In Protonic Media. A solution of 50 mg (0.26 mmol) of enedione **28** in 0.75 mL of methanol and 0.25 mL of 3% aqueous potassium hydroxide was stirred at room temperature for 27 h. The mixture was poured into 30 mL of methylene chloride–water (2:1). The organic layer was dried ($MgSO_4$) and concentrated to give 36 mg of a yellow oil containing two components by TLC. This material was subjected to thin-layer chromatography over silica gel (three elutions with benzene–ethyl acetate, 1:1) to give 5 mg (10%) of ketol **27** and 21 mg (42%) of recovered enedione **28**. Under identical conditions (concentration, time, temperature), ketol **27** was recovered unchanged. Vinyl alcohol **3** rearranged to **27** (60%) and **28** (4%) in 4 h under these conditions.

(B) In Deuteronic Media. A solution of 192 mg (1.0 mmol) of **28** in 2.0 mL of methanol-d_1 containing 13 mg of dissolved sodium metal was allowed to stand at room temperature for 96 h. The mixture was poured into ether–water. The organic layer was dried ($MgSO_4$) and concentrated to give 131 mg of a yellow oil. This material was chromatographed over 10 g of silica gel (eluted with benzene–ethyl acetate, 85:15) to give 49 mg (26%) of polydeuterated **27**. This material had incorporated deuterium at carbons 2, 4, 6, 9, 11, and 12 by ^{13}C NMR analysis.

7α-Ethynyl-7β-hydroxy-3,7aβ-dimethyl-2,4,5,6,7a-hexahydroinden-2-one (35). To a solution of lithium acetylide, prepared in the usual manner from 21 mg (3.0 mmol) of lithium and acetylene in 25 mL of liquid ammonia, was added 190 mg (1.07 mmol) of dione **20** in 10 mL of ether over a 20-min period. The resulting solution was stirred for an additional 40 min followed by the addition of 168 mg (3.0 mmol) of ammonium chloride in 5 mL of water. The ammonia was allowed to evaporate and the residue was partitioned between ether and water. The ether layer was dried ($MgSO_4$) and concentrated. The residual solid was recrystallized from carbon tetrachloride–ethyl acetate to give 130 mg (60%) of analytically pure alcohol **35** as tiny plates: mp 141–144 °C; UV λ_{max} (MeOH) 242 nm (ϵ 8900); IR ($CDCl_3$) 3600, 3360, 3300, 1690, 1645, cm^{-1}; NMR ($CDCl_3$) δ 1.30 (s, 3), 1.70 (s, 3), 1.8–3.2 (m, 10); MS (70 eV) *m/e* 204 (M$^+$), 189, 186, 161, 148, 39 (base).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.19; H, 7.67.

7β-Hydroxy-3,7aβ-dimethyl-7α-vinyl-2,4,5,6,7,7a-hexahydroinden-2-one (36). A solution of 120 mg (0.59 mmol) of ethynyl alcohol **35** in 2.0 mL of pyridine was hydrogenated at room temperature and 1 atm over 20 mg of 5% palladium on barium sulfate until 14 mL (1 equiv) of hydrogen had been consumed. The solution was diluted with dichloromethane, filtered through Celite, washed thoroughly with 10% aqueous HCl, and concentrated. The residual solid was recrystallized from carbon tetrachloride–hexane to give 83 mg (70%) of analytically pure vinyl alcohol **36**: mp 98.5–99.5 °C; UV λ_{max} (MeOH) 244 nm (ϵ 7000); IR (CCl_4) 3400, 1700, 1655, 990, 935 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (s, 3), 1.68 (s, 3), 1.7–2.8 (m, 9), 4.9–6.00 (12 line ABC system, 3); MS (70 eV) *m/e* 206 (M$^+$), 188, 136 (base).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.85; H, 8.71.

4,7-Dimethyltricyclo[6.3.0.0^{4,8}]undec-6-en-5-on-1-ol (37). A solution of 80 mg (0.39 mmol) of vinyl alcohol **36** in 1.28 mL of methanol and 0.42 mL of 3% aqueous potassium hydroxide was warmed at 60 °C for 90 min. The mixture was poured into a few milliliters of ether–water (1:1). The organic layer was separated and the aqueous layer was extracted with ether. The combined ether solutions were dried ($MgSO_4$) and concentrated to afford 70 mg of a yellow oil. This oil was subjected to thin-layer chromatography on silica gel (eluted with benzene–ether, 1:1) to afford 54 mg (67%) of tricyclic ketol **37**. Analytically pure material (40 mg) was crystallized from carbon tetrachloride–ether: mp 98–101 °C; UV λ_{max} (MeOH) 245 nm (ϵ 8300); IR (CCl_4) 3400, 1707, 1605 cm^{-1}; NMR (CCl_4) δ 0.93 (s, 3), 1.2–2.3 (m, 13, with d, J = 1.5 Hz, at 2.15), 2.83 (br s, 1), 5.79 (q, 1, J = 1.5 Hz); MS (70 eV) *m/e* 206 (M$^+$), 191, 188, 178, 163, 160, 145, 122 (base).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 75.69; H, 8.80. Found: C, 75.92; H, 8.64.

Registry No.—3, 63702-34-1; **4,** 63702-35-2; **7,** 32561-57-2; **10,** 32561-55-0; **11,** 63702-36-3; **12,** 63702-37-4; **13,** 63702-38-5; **14,** 63702-39-6; **15,** 63702-40-9; **16,** 63702-41-0; **17,** 63702-42-1; **18,** 63702-43-2; **19,** 63702-44-3; **20,** 63702-45-4; **24,** 63702-46-5; **25,** 63702-47-6; **26,** ,63702-48-7; **27,** 63702-49-8; **28,** ,63702-50-1; **29,** 63702-51-2; **30,** 63702-52-3; **31,** 63702-53-4; **31**-d_3, 63702-54-5; **32,** 63702-55-6; **32**-d_3, 63702-56-7; **33,** 63702-57-8; **35,** 63702-58-9; **36,** 63702-59-0; **37,** 63702-60-3; 2-methylcyclohexane-1,3-dione, 1193-55-1; propargyl bromide, 106-96-7; ethylene glycol, 107-21-1; acetylene, 74-86-2; benzyl 2-bromoacetate, 40796-37-0.

References and Notes

(1) This research was supported by the National Science Foundation, Grant No. MPS 73-04662, and by the Hoffmann-LaRoche Foundation.

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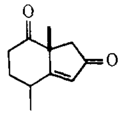
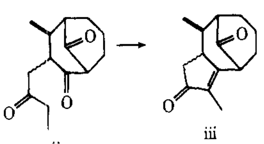
(12) This reaction sequence was also applied to an unsymmetrical cyclohexane-1,3-dione to illustrate the applicability of this route to the synthesis of analogues of **4.** Therefore, it was possible to convert 2,4-dimethylcyclohexane-1,3-dione to enone i using the reaction sequence outlined above.



i

(13) As noted above, omission of the crown ether merely resulted in a quantitative recovery of starting material. Using KF and 18-crown-6, we have also been able to effect conversion of ii to iii in 50% yield. This reaction also fails under several of the aforementioned reaction conditions due to cleavage of the acid and base labile bicyclo[3.3.1]nonane-2,9-dione system. The formation of mesityl oxide during KI-dibenzo-18-crown-6 displacements in acetone has been reported: D. J. Sam and H. E. Simmons, *J. Am. Chem. Soc.*, **96,** 2252 (1974).



ii iii

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(20) Over a number of runs during which concentration of the reactants, temperature, and reaction time were varied, the yield of **27** ranged from 35 to 65%, while the yield of **28** ranged from 4 to 8%. Reproducible yields were obtained using the conditions described in the text. During one run when **3** was rearranged with dimysl anion in Me_2SO a 65% yield of **27** was isolated.

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Photochemistry of Epoxyquinones. 1. Photochemical Reactions of 2-Alkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones with Hydrogen Donors[1]

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The photochemical reactions of 2-alkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones with good hydrogen donors such as xanthene or 2-propanol gave 2-alkyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinones, 2-alkyl-3-hydroxyl-1,4-naphthoquinones, and 9,9′-bixanthenyl as the main products. For example, the photochemical reaction of 2-methyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (**1b**) with xanthene gave 2-methyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone (**3b**), 2-methyl-3-hydroxy-1,4-naphthoquinone (**4b**), 9,9′-bixanthenyl (**5**) and 3,3′-bis(2-methyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone) (**6**). Isotope effects and the effect of the molar ratio of the reactants on the products distribution suggested that the products **3b** and **6** were formed by hydrogen abstraction of **1b** from xanthene, but the product **4b** was formed by intramolecular rearrangement. The photolysis of 2-methyl-2-hydroxy-3-(9′-xanthenyl)-2,3-dihydro-1,4-naphthoquinone in the absence or in the presence of xanthene also gave the product **3b** or **4b,** respectively, suggesting that the products **3b** and **4b** were formed from the same radical intermediate **10.** The reaction of 2-methyl-2,3-epoxy-3,4-dihydro-4-hydroxynaphthalen-1(2*H*)-one with di-*tert*-butyl peroxalate also gave the product **3b,** together with the epoxyquinone **1b,** suggesting that the product **3b** was also formed by the ring opening rearrangement of the intermediate radical **8.** The photochemical reaction was examined by means of CIDNP. From these data, the reaction mechanism for the formation of the products **3b, 4b, 6,** and **5** is presented.

The photochemistry of α,β-epoxy ketones has been well studied in the past.[2] However, little attention has been paid to the photochemistry of epoxyquinones. In this paper we wish to report the photochemical reactions of 2-alkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones in the presence of good hydrogen donors. For this work we prepared seven epoxyquinones **1a–g,** and examined their photochemical reactions with hydrogen donors such as xanthene or 2-propanol.

Results and Discussion

Photoreduction of 2-Alkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones with Xanthene or 2-Propanol. A solution of 2-alkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones (0.03–0.06 M) and 2 equiv of xanthene in benzene was irradiated in a Pyrex test tube for 10–50 h, using a 300-W high-pressure mercury lamp. Separation of the products by column chromatography and preparative TLC gave 2-alkyl-