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Annelative Ring Expansion via Intramolecular [2 + 2] Photocycloaddition of α,β-Unsaturated γ-Lactones and Reductive Cleavage: Synthesis of Hydrocyclopentacyclooctene-5-carboxylates

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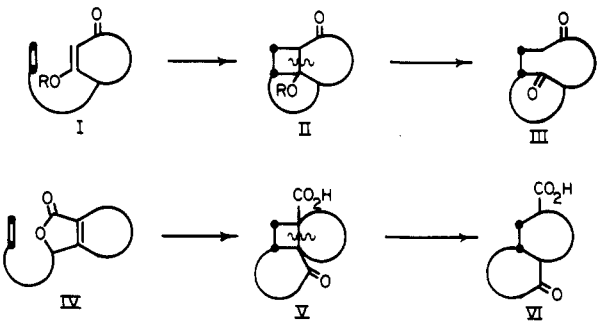
A new approach for annelative, two-carbon ring expansion via intramolecular [2 + 2] photocycloaddition of fused α,β-unsaturated γ-lactones onto γ-alkenyl side chains, oxidation to γ-keto acids, and reductive cleavage of the cyclobutane ring is applied to the synthesis of hydrocyclopentacyclooctene-5-carboxylates. α,β-Unsaturated γ-lactones fused to cyclohexene and bearing 3-butenyl (**4**), 3-pentenyl (**5**), 3,4-pentadienyl (**7**), and 4-chloro-3-pentenyl (**9**) side chains in the γ-positions were prepared (Schemes II and III) either by addition of Grignard reagents to 2-bromo-1-cyclohexenecarboxaldehyde (**1**) followed by lithiation and carboxylation (method A) or by lithiation of *N,N*-dimethyl-2-bromo-1-cyclohexenecarboxamide (**6**) and subsequent addition to aldehydes (method B). Irradiation of the four unsaturated lactones effected mainly the fused mode of intramolecular [2 + 2] cycloaddition, forming 2-hydroxytricyclo[5.4.0.0^{1,5}]undecane-7-carboxylic acid lactones (**13–15** and **17**). Oxidation of the sodium salts of the hydroxy acids with sodium ruthenate and esterification afforded a series of tricyclic γ-keto acids (**20a** and **21a**) and esters (**20b** and **22**). Reduction of the keto acids or esters with lithium in ammonia lead to reductive scission of the cyclobutane ring and formation of methyl decahydro- and octahydro-1-oxo-1*H*-cyclopentacyclooctene-5-carboxylates (**24–26**).

Intramolecular [2 + 2] photocycloaddition of cyclic α,β-enones with remote double bonds has become an important synthetic method for the construction of polycyclic ring systems.[1] When combined with subsequent cleavage of the α,β bond in the cyclobutane ring by retroaldol, retro-Prins, or reductive fragmentation, the overall transformation constitutes an annelative two-carbon ring expansion of the original enone.[2,3] The intramolecular de Mayo reaction[2a-c,4] (I → II → III; Scheme I) is one example of this annelation method. We have developed a new variation (IV → V → VI) of this strategem which begins with intramolecular photochemical [2 + 2] cycloaddition of fused α,β-unsaturated γ-lactones bearing alkenyl side chains in the γ-position.[5] Oxidation of the resulting cyclobutylcarbinol to a γ-keto acid followed by reductive cleavage of the cyclobutane ring gives rise to bicyclic ε-keto acids with differentially functionalized rings. We herein report the application of this annelation procedure to the synthesis of hydrocyclopentacyclooctene-5-carboxylates,[6] compounds which bear a structural resemblance to the A/B rings of the fusicoccin and ophiobolane natural products.[7]

Scheme I



(1) (a) Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123–225. (b) Meier, H. In "Methoden der Organische Chemie (Houben-Weyl)"; E. Muller, Ed.; Georg Thieme Verlag: Stuttgart, 1975; Vol. 4/5b, pp 932–941. (c) Dilling, W. L. *Chem. Rev.* **1966**, *66*, 373–393.

(2) (a) Oppolzer, W.; Godel, T. *J. Am. Chem. Soc.* **1978**, *100*, 2583–84. (b) Begley, M. J.; Mellor, M.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1979**, 235–36. (c) Oppolzer, W.; Bird, T. G. C. *Helv. Chim. Acta* **1979**, *62*, 1119–1202. (d) Oppolzer, W.; Wylie, R. D. *Ibid.* **1980**, *63*, 1198–1203. (e) Eaton, P. E. *Tetrahedron*, **1979**, *35*, 2189–2223; (f) Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135–141.

(3) For review on two-carbon ring expansion, see (a) Gutsche, C. D.; Redmore, D. "Carbocyclic Ring Expansion Reactions"; Academic Press: New York, 1968; pp 161–189. (b) Hiyama, T.; Nozaki, H. *J. Synth. Org. Chem. Jpn.* **1977**, *35*, 979–91.

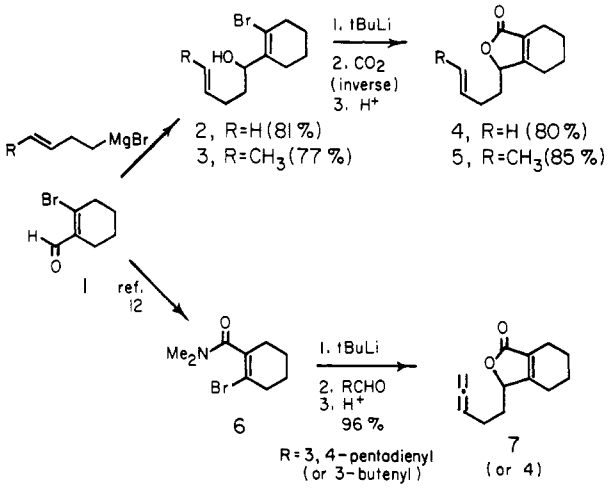
(4) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41–7.

(5) Some examples of intramolecular [2 + 2] photocycloaddition of butenolides have been reported recently: Pearlman, B. A. *J. Am. Chem. Soc.* **1979**, *101*, 6398–6404, 6404–6408.

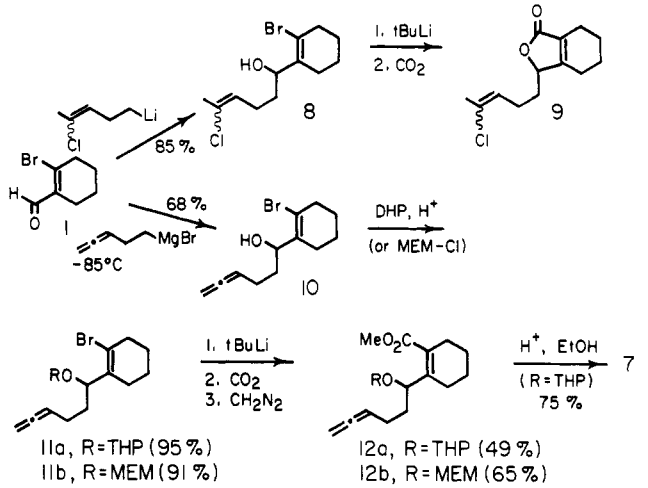
(6) Baker, W. R.; Senter, P. D.; Coates, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 1011–12.

0022-3263/82/1947-3597$01.25/0

Scheme II



Scheme III



α,β-Unsaturated γ-lactones fused to a cyclohexene ring[8] and substituted with various alkenyl groups in the γ-position were prepared by two different routes as shown in Scheme II. Both originate from 2-bromo-1-cyclohexenecarboxaldehyde (1), which is available from cyclohexanone by the bromo analogue of the Vilsmeier reaction according to the procedure of Arnold and Holy.[9] Addition of the Grignard reagents derived from 4-bromo-1-butene and a 9:1 *E*/*Z* mixture of the 5-bromo-2-pentene isomers[10] to bromo aldehyde 1 in a tetrahydrofuran (THF) gave bromo alcohols 2 and 3 (method A). The IR and carbon-13 NMR spectra of 3 confirmed that the side-chain double bond was *E* and that no more than 5–10% of the *Z* isomer was present. Carboxylation of the vinyllithium reagents generated from the bromo alcohols by bromine–lithium exchange with 3.5 equiv of *tert*-butyllithium in THF[11] at −100 to −45 °C afforded butenolides 4 and 5 in 80–85% yield. These high yields of the lactones were reproducibly obtained by an inverse addition procedure in which the THF solution of the metalated intermediate was added via cannula transfer to a solution of carbon dioxide in THF at −78 °C. When excess carbon dioxide was introduced into a solution of organolithium reagent in the normal manner, the yield of the lactone was quite low in some runs, evidently owing to formation of the *tert*-butyl cyclohexenyl ketone from reaction with excess *tert*-butyllithium.

The second method used to prepare the fused butenolides involved reaction of *N*,*N*-dimethyl-2-lithio-1-cyclohexenecarboxamide with aldehydes (method B).[12] Lithiation of bromo amide 6 with 2.2 equiv of *tert*-butyllithium in THF at −70 to −75 °C followed by addition of 2.3 equiv of 4-pentenal at −60 °C and hydrolysis with 25% aqueous acetic acid afforded butenyl lactone 4 in 68% yield based on 6. The 3,4-pentadienyl lactone 7 was formed in a similar manner from 6 and 4,5-hexadienal, except that 1.5 equiv of the lithiated amide was employed with respect to the aldehyde reactant. 4,5-Hexadienal was prepared both by reduction of 4,5-hexadienenitrile with diisobutylaluminum hydride (34%) and by oxidation of 4,5-hexadien-1-ol in pentane with the aza sulfonium salt formed from *N*-chlorosuccinimide and dimethyl sulfide (32%).[13] The nitrile was obtained by displacement of the *p*-toluenesulfonate[14] of 3,4-pentadien-1-ol[15] with cyanide ion (76%). The following sequence of reactions was employed for the preparation of 4,5-hexadien-1-ol[16] from 4-penten-1-ol (overall yield, 14%): silylation with hexamethyldisilazane (95%),[17] dibromocyclopropanation with phenyl(tribromomethyl)mercury (52% based on the organomercurial),[18] carbenoid ring opening with methyllithium (85%),[19] and hydrolysis of the trimethylsilyl group (81%).

Lactone 9 bearing a chloropentenyl substituent was readily prepared by method A (Scheme III). (4-Chloro-3-pentenyl)lithium[20] generated from the corresponding iodide[21] by exchange with *tert*-butyllithium reacted with bromo aldehyde 1 to give bromo alcohol 8. Lithiation of the vinyl bromide and carboxylation by the inverse addition procedure afforded chloropentenyl lactone 9 as a 2.4:1 mixture of *Z* and *E* isomers.

An alternative synthesis of the pentadienyl lactone 7 by a variation of method A was also developed (Scheme III). Bromo alcohol 10 was readily obtained by addition of 3,4-pentadienylmagnesium bromide to bromo aldehyde 1. The Grignard reagent was generated at low temperature from 5-bromo-1,2-pentadiene with highly reactive magnesium according to the procedure of Rieke and co-workers[22] so as to avoid cyclization.[23] Attempts to convert 10

(7) (a) Cordell, G. A. *Phytochemistry* **1974**, *13*, 2343–64. (b) Canonica, L.; Fiecchi, A. *Res. Prog. Org.-Biol. Med. Chem.* **1970**, *2*, 49–93. (c) Cordell, G. A. *Prog. Phytochem.* **1977**, *4*, 209–56.

(8) *Chemical Abstracts* indexes these compounds as derivatives of 4,5,6,7-tetrahydro-1(3*H*)-isobenzofuranone.

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(10) Julia, M.; Julia, S.; Tchen, S.-Y. *Bull. Soc. Chim. Fr.* **1961**, 1849–53.

(11) An extra equivalent of *tert*-butyllithium is required to destroy *tert*-butyl bromide formed by lithium–bromine exchange. See Seebach, D.; Newman, H. *Chem. Ber.* **1974**, *107*, 847–53.

(12) Baker, W. R.; Coates, R. M. *J. Org. Chem.* **1979**, *44*, 1022–24.

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(16) Ragonnet, B.; Santelli, M.; Betrand, M. *Bull. Soc. Chim. Fr.* **1973**, 3119–21.

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(19) Skattebøl, L.; Solomon, S. In "Organic Syntheses", Collect. Vol. V; Wiley: New York, 1973; pp 306–310.

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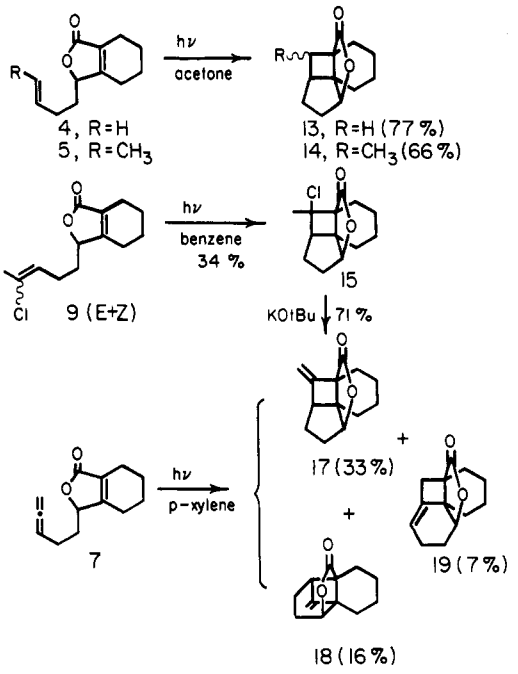
(21) Kreiser, W.; Janitschke, L. *Chem. Ber.* **1979**, *112*, 408–22.

(22) Rieke, R. D.; Bales, S. E.; Hudnall, P. M.; Poindexter, G. S. *Org. Synth.* **1980**, *59*, 85–94. We thank Professor Samuel Danishefsky for providing a procedure for the formation of 3,4-pentadienylmagnesium bromide in this manner.

(23) Richey, H. G., Jr.; Kossa, W. C., Jr. *Tetrahedron Lett.* **1969**, 2313–4.

Scheme IV

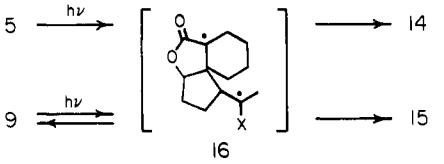


directly to the lactone by lithiation with *tert*-butyllithium and carboxylation were not successful. Since complex mixtures of products lacking the allene group were obtained, it appeared that the allene was not stable to the metalation conditions. It was necessary to raise the temperature to −45 °C to effect complete lithiation of the heterogeneous mixture of lithium salts formed initially from the bromo alcohols at −90 °C. However, lithiation of the corresponding tetrahydropyranyl (THP) or (methoxyethoxy)methyl (MEM) ethers[24] (**11a** and **11b**) was complete within a few minutes at −100 to −80 °C. Immediate carboxylation of the resulting vinyllithium with carbon dioxide followed by hydrolysis and diazomethane esterification provided methyl esters **12a** and **12b**. The moderate yields of these reactions (49% and 65%, respectively) probably reflect some competitive destruction of the allene group. Although deprotection of the methoxyethoxymethyl ether **12a** with either zinc bromide or titanium tetrachloride in dichloromethane[24] afforded lactone **7** in low yield, ethanolysis of the tetrahydropyranyl group of **12b** with pyridinium *p*-toluenesulfonate[25] as catalyst produced the desired lactone in 75% yield. The overall yield of **7** from bromo aldehyde **1** was 24%.

The intermolecular photochemical [2 + 2] cycloaddition of various α,β-unsaturated γ- and δ-lactones have been studied.[5,26] Since the cycloaddition of α,β-butenolide and cyclopentene was sensitized by acetone and quenched by 1,3-pentadiene, it was concluded that the reaction proceeds through the triplet state of the lactone.[26a]

Irradiation of lactones **4** and **5** in acetone in quartz vessels afforded tricyclic lactones **13** and **14** in good yield (Scheme IV). GC analyses and NMR spectra indicated that the photoproduct from **5** was a 1:1.6 mixture of stereoisomers. The fused tricyclo[5.4.0.0^{1,5}]undecane structures assigned to the photo lactones **13** and **14** are based upon IR spectral data for the keto acids and esters obtained from the ruthenate oxidations described below. Although no evidence for the formation of the isomeric photoproducts with bridged ring structures was obtained, small amounts of these compounds might have escaped detection. The photocycloaddition of the chloropentenyl lactones **9** in benzene proceeded at least 50 times more slowly than that of **5**. A single crystalline photoproduct (**15**) was isolated in 34% yield following chromatographic purification. Irradiations of **9** conducted in acetone and *p*-xylene were also quite sluggish and appeared to be less efficient.

The formation of C-6 epimers from the irradiation of (*Z*)-3-pentenyl lactone **5** may be explained by assuming that rotation about the exocyclic C–C bond in a diradical intermediate (**16**, X = H) is competitive with ring closure. Rapid reversion of the chloro diradical (**16**, X = Cl) to starting lactone **9** may be responsible for the slow rate of this irradiation. Intermolecular photochemical [2 + 2] cycloaddition reactions between cyclic enones and chloro alkenes have been reported.[27]



In contrast to the apparently high regioselectivity observed in the photocycloadditions of the butenyl- and pentenyl-substituted lactones **4**, **5**, and **9**, irradiation of the 3,4-pentadienyl lactone **7** in *p*-xylene afforded a 2:1 ratio of fused and bridged cycloadducts **17** and **18** as major products, which were separated by medium-pressure liquid chromatography. A small amount of a third photoproduct (**19**) resulting from cycloaddition to the terminal double bond of the allene was also isolated. The structure of **19** is evident from its NMR spectrum, which exhibits a single vinyl proton at δ 5.58. The NMR spectra of **17** and **18** each display two well-separated peaks attributable to the protons of the exocyclic methylene groups. Lower yields of **17** and **18** were obtained when acetone, hexane, or benzene were tried as solvents for the irradiation. The fused structure of the photoproduct from **9** was confirmed by dehydrochlorination to **17** with potassium *tert*-butoxide in THF.

Before reductive cleavage of the C1–C7 bond of the tricyclic lactones could be attempted, it was first necessary to hydrolyze and oxidize the compounds to the corresponding γ-keto acids. This transformation was, however, complicated by the facile relactonization of the hydroxy acids and esters. Although partial esterification of the sodium salt from saponification of lactone **13** was accomplished with trimethyloxonium fluoroborate in water,[28] oxidation of the resulting hydroxy ester with the chromium trioxide–bipyridine complex in dichloromethane[29] afforded a mixture of the desired keto ester (**20b**) and recovered lactone. An attempt to oxidize the tetrabutylammonium salt of the hydroxy acid by the same procedure gave keto acid **20a** in only 5% yield. Reaction of the sodium salt with *p*-bromophenacyl bromide in dimethylformamide[30] lead to relactonization during either the esterification or the subsequent evaporation of the solvent at 0 °C. Oxidation

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(25) Miyashita, N.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772–74.
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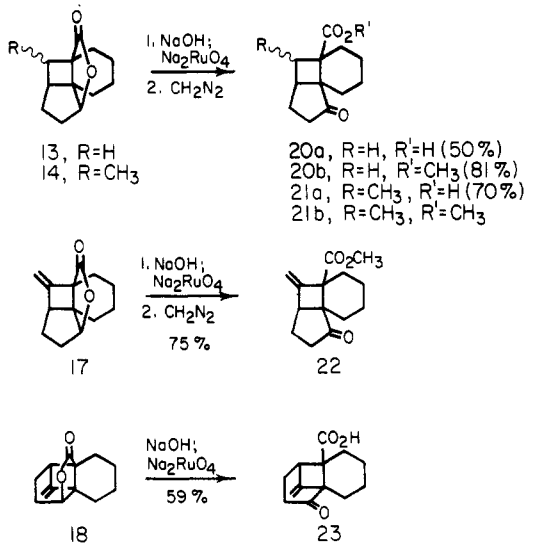
(27) (a) House, H. O.; Cronin, T. H. *J. Org. Chem.* **1965**, *30*, 1061–70. (b) Cargill, R. L.; King, T. Y.; Sears, A. B.; Willcott, M. R. *Ibid.* **1971**, *36*, 1423–8.
(28) Hamada, T.; Yonemitsu, O. *Chem. Pharm. Bull.* **1971**, *19*, 1444–9.
(29) Ratcliffe, R.; Rodehurst, R. *J. Org. Chem.* **1970**, *35*, 4000–2.
(30) Hendrickson, J. B.; Bogard, T. L.; Fisch, M. E.; Grossert, S.; Yoshimura, N. *J. Am. Chem. Soc.* **1974**, *96*, 7781–9.

Scheme V



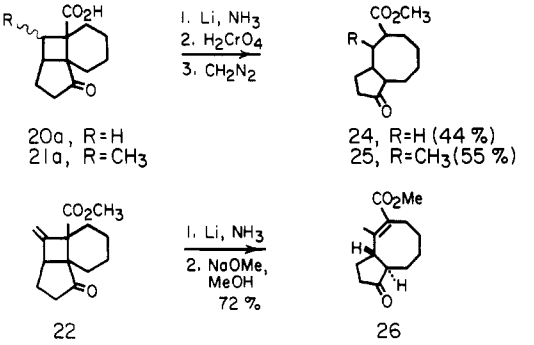
of the sodium salt with chromium trioxide in aqueous pyridine[31] gave the keto acid in 40% yield along with recovered lactone.

Efficient conversion of the lactones to the required keto acids was eventually realized by oxidation of their sodium salts with sodium ruthenate in water[32] as shown in Scheme V. Aqueous solutions of sodium ruthenate were prepared by extraction of ruthenium tetraoxide in carbon tetrachloride with 1 M sodium hydroxide. Addition of 1.1 equiv of aqueous sodium ruthenate to aqueous solutions of the sodium salts from saponification of the lactones resulted in the immediate precipitation of ruthenium dioxide and apparently rapid oxidation of the keto carboxylates. The keto acids were either isolated and purified (50–70% yields) or immediately esterified with diazomethane to form the keto esters (59–81%).

The assignment of the fused tricyclo[5.4.0.0^{1,5}]undecane structures to the photo lactones **13**, **14**, and **17** is based principally upon the carbonyl stretching frequencies observed in the IR spectra of the derived keto acids and/or esters. The appearance of this absorption peak in the range 1724–1736 cm^{-1} indicates the presence of a cyclopentanone ring in these compounds. In contrast, the IR spectrum of the keto acid (**23**) prepared from the minor photo lactone (**18**) obtained in the irradiation of 3,4-pentadienyl lactone **7** exhibited a carbonyl peak at 1709 cm^{-1} in accord with the presence of a cyclohexanone. The bridged tricyclo[5.3.1.0^{1,6}]undecane skeleton is therefore assigned to **18** and **23**.

The reductive fragmentation of strained rings bearing carbonyl groups in a 1,4-relationship is well precedented.[33] Keto acids **20a** and **21a** as well as keto ester **20b** were subjected to reduction with lithium in refluxing ammonia with THF as cosolvent in the presence and absence of *tert*-butyl alcohol as a proton source (Scheme VI). Since the reactions were invariably complicated by competing reduction of the cyclopentanone carbonyl group, the crude

Scheme VI



products were reoxidized with chromic acid in acetone[34] and esterified with diazomethane to facilitate chromatographic purification. Substantial amounts of the tricyclic keto esters **20b** (20%) and **21b** were recovered from the reductions of **20a** and **21a**. The expected methyl decahydro-1-oxo-1*H*-cyclopentacyclooctene-5-carboxylates **24** (44%) and **25** (55%) proved to be the major products of these reductions and were obtained as mixtures of several isomers. The spectral data, GC–MS analyses, combustion analyses, and high-resolution mass spectra for the reduced keto esters are consistent with the gross bicyclic structures indicated. A somewhat lower yield of **24** (41%) was isolated from a reduction of keto ester **20b**.

Reduction of the unsaturated keto ester **22** afforded a multicomponent mixture of α,β- and β,γ-unsaturated esters according to GC analyses and NMR spectra. No carbonyl reduction occurred in this case. Equilibration of the isomer mixture with sodium methoxide in refluxing methanol effected conversion to a single conjugated ester **26** (72%), mp 72–73 °C, which was characterized by IR, NMR, and UV spectral data as well as high-resolution mass spectrometry. The stereochemistry of the ring juncture is assumed to be trans in analogy to related compounds having the same ring system.[2b,35]

Experimental Section

Melting points and boiling points are uncorrected. Spectra were recorded with the following instruments: Varian Associates Models EM-390 or HR-220 NMR spectrometers; Perkin-Elmer Models 137, 337, or Beckman Model 12 IR spectrometers; Varian MAT CH-5, 311A, or 731 mass spectrometers. Microanalyses were performed by Mr. Josef Nemeth and associates at the University of Illinois Microanalytical Laboratory.

Gas–liquid chromatographic analyses were performed with Varian Models 3700 and A90-P3 gas chromatographs using the following columns: (A) 3% (1:1) methylphenylsilicone (OV-17) on Chromosorb Q 100/200 mesh, 1.8 m by 6.3 mm, (B) 3% OV-17 on Chromosorb Q 100/200 mesh, 3.6 m by 6.3 mm, (C) 20% OV-17 on Chromosorb P 60/80 mesh, 2.7 m by 9.5 mm, and (D) 20% silicone gum rubber (SE-30) on Chromosorb W 60/80 mesh, 2.7 m by 9.5 mm.

Chromatographic purifications at atmospheric pressure were performed on silica gel, using 20 cm × 20 cm × 2 mm preparative thin-layer plates or Brinkmann 0.05–0.20-mm silica particles packed in open-ended glass columns. Flash chromatography was performed by the procedure of Still and co-workers[36] on Woelm 32–63 μm silica gel supplied by Universal Scientific, Atlanta, GA. Preparative medium-pressure chromatography (MPLC) was carried out in glass columns packed with sieved silica gel.[12]

All reactions with the exception of aqueous oxidations were carried out in a nitrogen or argon atmosphere, using standard techniques for the exclusion of air and moisture. Glassware used

(31) (a) Cornforth, R. H.; Cornforth, J. W.; Popjak, G. *Tetrahedron* **1962**, *18*, 1351–4. (b) Wuonola, M. H.; Woodward, R. B. *Ibid.* **1976**, *32*, 1085–95.

(32) (a) Lee, D. G.; Hall, D. T.; Cleland, J. H. *Can. J. Chem.* **1972**, *50*, 3741–3. (b) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S.; Keck, G. E.; Gopalan, B.; Larsen, S. D.; Siret, P.; Gras, J. *J. Am. Chem. Soc.* **1978**, *100*, 8034–6.

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for water-sensitive reactions was dried in a circulating oven at 135 °C for at least 1 h and then flame-dried with an internal inert gas sweep.

Tetrahydrofuran, benzene, dioxane, and ether were purified and dried by distillation from sodium benzophenone ketyl. Ammonia was dried by distillation from sodium. All other solvents were reagent grade and purified as needed by use of standard literature procedures. Anhydrous carbon dioxide was used for all lactonization reactions and was obtained by sublimation through phosphorus pentoxide.

2-Bromocyclohexene-1-carboxaldehyde (1).[9] A mechanically stirred solution of 40.0 g (0.552 mol) of dimethylformamide in 150 mL of anhydrous chloroform was cooled in an ice bath while 135 g (0.497 mol) of phosphorus tribromide was added dropwise over a 15-min period. The resulting yellow suspension was warmed to room temperature and stirred an additional 20 min. A solution of 18 g (0.184 mol) of cyclohexanone in 50 mL of chloroform was added dropwise over 10 min, using a water bath to moderate the exothermic reaction. Stirring was continued for 12 h at room temperature after which the dark-red solution was poured into about 100 mL of ice water contained in a 1-L flask. Solid sodium bicarbonate was carefully added to neutralize the acids, and the mixture was extracted with several portions of ether. The combined ethereal extracts were washed with saturated sodium chloride, dried ($MgSO_4$), and evaporated. Purification of the residue by flash chromatography on a 60-mm column with 1:9 ethyl acetate–hexane as eluant furnished 12.08 g (35%) of bromo aldehyde 1 as a pale-yellow oil. The spectral data agree with those in the literature.[12]

Warning: In one instance bromo aldehyde 1 exploded after it had been stored about 1 month in a freezer at −20 °C and then allowed to warm to room temperature. The instability of 1 and related compounds have been noted in the literature.[9] It is best to prepare this compound immediately before use.

1-(2-Bromo-1-cyclohexenyl)-4-penten-1-ol (2). A 3-g (22 mmol) portion of 4-bromo-1-butene was added to 2.7 g (110 mmol) of magnesium turnings under 20 mL of tetrahydrofuran to initiate the formation of the Grignard reagent. When the mixture became warm, a solution of the remaining 9.1 g (67 mmol) of 4-bromo-1-butene in 60 mL of tetrahydrofuran was added over 20 min. The reaction was stirred for 18 h (2 h in another run) at room temperature after which the Grignard reagent was added to a solution of 14.0 g (74 mmol) of bromo aldehyde 1 in 30 mL of tetrahydrofuran at −40 to −50 °C. The resulting solution was allowed to warm to 20 °C, 25 mL of saturated sodium chloride was added, and the aqueous layer was extracted 3 times with ethyl ether. The combined ethereal extracts were washed with saturated sodium chloride, dried (Na_2CO_3), and evaporated to give 18.5 g of crude alcohol 2. Purification by MPLC with 1:2 diethyl ether–hexane furnished 15.1 g (83%) of alcohol 2. An analytical sample was prepared by Kughelrohr distillation at 0.1 mm with an oven temperature of 90–95 °C: IR (film) ν_{max} 3030–3570 (OH), 1634 (C=C) cm^{-1}; H NMR ($CDCl_3$) δ 1.40–1.80 (m, 6 H, 3 CH_2), 2.00 (s, 1 H, OH), 1.93–2.30 (m, 4 H, 2 allylic CH_2), 2.30–2.63 (m, 2 H, allylic CH_2), 4.70 (t, J = 7 Hz, 1 H, C=CCHOH), 4.80–5.13 (m, 2 H, CH=CH_2), 5.53–6.03 (10-line m, 1 H, CH=CH_2).

Anal. Calcd for $C_{11}H_{17}BrO$: C, 53.88; H, 7.00; Br; 32.59. Found: C, 53.84; H, 6.90; Br 32.72.

5-Bromo-2-pentene. The procedure of Julia and co-workers[10] was employed with a number of modifications. A suspension of 9.14 g (0.24 mol) of lithium aluminum hydride in 150 mL of anhydrous ether was rapidly stirred in a 500-mL, round-bottomed flask equipped with an efficient condenser while 40 g (0.48 mol) of cyclopropyl methyl ketone was added over 15 min. Excess hydride was destroyed by addition of 9.1 mL of water, 9.1 mL of 1 M sodium hydroxide, and 27.3 mL of water in succession. The granular aluminum salts were filtered and washed with several portions of ether. The solvent was distilled at atmospheric pressure through a 15-cm Vigreux column, leaving crude cyclopropylmethylcarbinol as an opaque colorless oil, which was used in the next step without further purification.

The crude alcohol was dissolved in 200 mL of 48% hydrobromic acid and rapidly stirred at 0 °C for 1.5 h. The mixture was extracted with several portions of ether. The combined ether extracts were washed with saturated sodium carbonate and saturated sodium chloride and dried ($MgSO_4$). The solvent was distilled at atmospheric pressure through a 15-cm Vigreux column. Distillation of the residue through the same column furnished 61.85 g (87%) of the bromide as a colorless liquid: bp 122–128 °C [lit.[10] bp 68–69 °C (102 mm)]. A GLC analysis on column B (temperature program, 50 °C 2 min, 20 °C/min to 150 °C) of the product indicated a 9:1 ratio of *trans* and *cis* isomers: ^1H NMR ($CDCl_3$) δ 1.68 (d, J = 6 Hz, 3 H, C=CCH_3), 2.53 (q, J = 6 Hz, 2 H, allylic CH_2), 3.35 (t, J = 8 Hz, 2 H, CH_2Br), 5.20–5.82 (11-line m, 2 H, HC=CH).

1-(2-Bromo-1-cyclohexenyl)-4-hexen-1-ol (3). A 2-mL portion of a solution of 3.51 g (23.8 mmol) of 5-bromo-2-pentene in 10 mL of tetrahydrofuran was added to 771 mg (31.74 mmol) of magnesium turnings in 50 mL of tetrahydrofuran. When the mixture became warm, the remainder of the 5-bromo-2-pentene solution was added dropwise over 15 min. The mixture was stirred for 2 h at room temperature to complete the formation of the Grignard reagent and then cooled to −90 °C. A solution of 3.00 g (15.87 mmol) of bromo aldehyde 1 in 10 mL of tetrahydrofuran was added via syringe. The cooling bath was removed, and the reaction mixture was warmed to room temperature. An excess of saturated ammonium chloride was added, and the mixture was extracted with several portions of ether. The combined ethereal extracts were washed with saturated sodium chloride, dried ($MgSO_4$), and evaporated. Purification by MPLC with 3:7 ether–hexane furnished 3.18 g (77%) of alcohol 3 as a colorless viscous oil: IR (film) ν_{max} 3300 (OH), 1645 (C=C), 967 (trans CH=CH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.51–1.80 (br s, $W_{1/2}$ = 12 Hz, 10 H, C=CCH_3, 3 CH_2, OH), 1.90–2.36 (m, 4 H, 2 allylic CH_2), 2.36–2.63 (m, 2 H, allylic CH_2), 4.77 (br t, J = 7 Hz, 1 H, CHOH), 5.47 (br s, $W_{1/2}$ = 12 Hz, 2 H, 2 C=CH); ^{13}C NMR ($CDCl_3$) δ 120.32, 125.52, 130.68, 137.50 (vinyl carbons).

Anal. Calcd for $C_{12}H_{19}BrO$: C, 55.60; H, 7.40; Br, 30.83. Found: C, 55.58; H, 7.63; Br, 30.94.

4-Pentenal. A. By Oxidation with Pyridinium Chlorochromate. To a mechanically stirred suspension of 32.2 g (150 mmol) of pyridinium chlorochromate in 200 mL of dichloromethane in a 1-L Morton flask was added 8.6 g (100 mmol) of 4-penten-1-ol. The mixture was stirred for 1.5 h and then filtered through 100 g of 60/100 mesh Florisil. The tarry residue in the flask was washed 3 times with ether, and the ether washes were filtered through Florisil. The combined filtrate was concentrated by distillation through a 15.2-cm Vigreux column at atmospheric pressure. Distillation of the remaining liquid at atmospheric pressure gave 3.5 g (41%): bp 103–110 °C [lit.[37] bp 101–105 °C]; IR (film) ν_{max} 1725 (C=O), 1637 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30–2.80 (m, 4 H, CH_2CH_2), 5.06–5.36 (m, 2 H, CH=CH_2), 5.80–6.30 (8-line m, 1 H, CH=CH_2), 10.13 (s, 1 H, CHO).

B. By Oxidation with Dimethyl Sulfide–*N*-Chlorosuccinimide. The oxidation of 3.34 g (40 mmol) of 4-penten-1-ol with 8.0 g (60 mmol) of *N*-chlorosuccinimide, 6 mL (100 mmol) of dimethyl sulfide, and 6.0 g (60 mmol) of triethylamine was carried out as described for the oxidation of 4,5-hexadien-1-ol (see below). Distillation at atmospheric pressure through a 15.2-cm column packed with glass beads gave 44 mL of a pentane solution containing 23 mmol (58%) of 4-pentenal based on NMR analysis, which was used in part B of the following procedure.

3-(3-Butenyl)-4,5,6,7-tetrahydro-1(3*H*)-isobenzofuranone (4). A. From Bromo Alcohol 2. A solution of 0.400 g (1.63 mmol) of bromo alcohol 2 in 4 mL of anhydrous tetrahydrofuran was cooled to −90 °C and stirred while 3.50 mL (5.71 mmol) of 1.63 M *tert*-butyllithium in pentane was added over 10 min. After 30 min, the solution was warmed to −45 °C over 15 min, stirred at this temperature for 1 h, and then transferred via double-pointed cannula to a solution of excess anhydrous carbon dioxide in 10 mL of tetrahydrofuran at −78 °C. The solution was warmed to room temperature and poured into 20 mL of ice-cold 10% hydrochloric acid. The aqueous layer was extracted three times with ether. The combined organic solutions were washed with saturated sodium bicarbonate and saturated sodium chloride, dried ($MgSO_4$), and evaporated. Purification of the product by chromatography on a 20-g column of silica gel with 1:4 ether–hexane as eluant afforded 250 mg (80%) of lactone 4 as a colorless oil with the following spectral characteristics: IR (film) ν_{max} 1750

(37) Webb, R. F.; Duke, A. J.; Parsons, J. A. *J. Chem. Soc.* **1961**, 4092–95.

(C=O), 1680 (C=C), 1645 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38–1.98 (m, 6 H, 3 CH_2), 1.98–2.40 (m, 6 H, 3 allylic CH_2), 4.76–5.20 (m, 3 H, CH=CH_2), 5.50–6.00 (m, 1 H, CH=CH_2).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.84; H, 8.45.

B. From Bromo Amide 6. An 11.0-mL (22 mmol) aliquot of a 2.0 M solution of *tert*-butyllithium in pentane was added to stirred solution of 2.3 g (10 mmol) of bromo amide **6**[12] in 20 mL of THF at −70 to −75 °C. After 1 h a solution of 23 mmol of 4-pentenal in 44 mL of pentane prepared as described above in method B was added at a rate to maintain the internal temperature below −60 °C. After 5 min, 10 mL of 25% aqueous acetic acid was added, and the mixture was allowed to warm to room temperature. Most of the organic solvents were removed by rotary evaporation, solid sodium chloride was added, and the aqueous mixture was extracted 3 times with ether. The combined extracts were washed with 10% hydrochloric acid, saturated sodium bicarbonate, and water. Drying ($MgSO_4$) and evaporation of the ethereal solution gave 2.3 g of crude lactone **4**. Purification by MPLC with 3:7 ethyl ether–hexane as eluent provided 1.3 g (68%) of lactone **4**, which was identical with the product obtained in A.

3-(3-Pentenyl)-4,5,6,7-tetrahydro-1(3*H*)-isobenzofuranone (5). A solution of 4.68 g (18.07 mmol) of bromo alcohol **3** in 150 mL of anhydrous tetrahydrofuran was cooled to −100 °C and stirred while 35.30 mL (63.24 mmol) of 1.79 M *tert*-butyllithium in pentane was added over 40 min. Toward the end of the addition period, a solid began to accumulate on the wall of the flask. The mixture was warmed to −45 °C and the solid gradually dissolved. Stirring was continued at −45 °C for 1.5 h after which the solution was transferred via a double-pointed cannula to a solution of excess anhydrous carbon dioxide in 10 mL of tetrahydrofuran at −78 °C. The solution was warmed to room temperature and poured into ice-cold 10% hydrochloric acid. The aqueous layer was extracted with three portions of ether. The combined organic solutions were washed with saturated bicarbonate and saturated sodium chloride, dried ($MgSO_4$), and evaporated. Purification of the product by flash chromatography on a 40-mm column with 1:4 ethyl acetate–hexane as eluant afforded 3.15 g (85%) of lactone **5** as a colorless viscous oil: IR (film) ν_{max} 1755 (C=O), 1680 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32–1.94 (m, 9 H), 1.94–2.38 (m, 6 H, 3 allylic CH_2), 4.78–4.92 (m, 1 H, CHOR), 5.33–5.54 (m, 2 H, HC=CH).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.68; H, 8.81. Found: C, 75.61; H, 8.79.

2-Penten-4-yn-1-ol was prepared from 100 g (1.05 mol) of lithium acetylide–ethylenediamine complex and 48.65 g (0.52 mol) of epichlorohydrin by the procedure of Sherrod and Bergman.[15c] The yield was 27.5 g (64%) of 2-penten-4-yn-1-ol as a 1:2 mixture of cis and trans isomers: bp 67 °C (7 mm) [lit.[15b] bp 65–66 °C (12 mm)]. The IR and NMR properties of the product agree with the reported data.

3,4-Pentadien-1-ol was prepared from 11.1 g (135 mmol) of 2-penten-4-yn-1-ol by the procedure of Sherrod and Bergman except that the acetylenic byproduct was removed by extractions with silver nitrate–ammonia.[15c] (See also ref 43.) The product was isolated by ether extraction, and the combined ether extracts were concentrated to a volume of 50 mL by distillation at atmospheric pressure through a 15.2-cm Vigreux column. The concentrate was washed 3 times with silver nitrate–ammonia solution before drying ($MgSO_4$). The ethereal solution was concentrated further by distillation at atmospheric pressure through a 15.2-cm Vigreux column, and the remaining liquid was distilled under reduced pressure, giving 6.7 g (60%) of 3,4-pentadien-1-ol: bp 57–58 °C (14 mm) [lit.[15b] bp 48 °C (10 mm)]; IR (film) ν_{max} 2500–3700 (OH), 1950 (C=C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3 (9-line m, J = 4 Hz, 2 H, CH_2), 2.66 (br s, 1 H, OH), 3.66 (t, J = 7 Hz, 2 H, CH_2OH), 4.66 (overlapping d of t, J = 3, 6 Hz, 2 H, CH=C=CH_2), 5.08 (overlapping d of t, J = 6, 12 Hz, 1 H, CH=C=CH_2).

4,5-Hexadienenitrile. A solution of 37.5 g (196 mmol) of *p*-toluenesulfonyl chloride and 15.0 g (178 mmol) of 3,4-pentadien-1-ol in 55 mL of pyridine was prepared at 0 °C and then stored at −25 °C for 36 h. The contents of the flask were poured into 200 mL of an ice–water mixture, and the aqueous suspension was extracted 3 times with ether. The combined ether extracts were washed once with saturated copper sulfate, once with water, and twice with 5% sodium bicarbonate. The ethereal solution was dried ($MgSO_4$) and evaporated, affording 40.6 g of the known tosylate.[14] A suspension of 12.05 g (246 mmol) of sodium cyanide in 120 mL of dimethyl sulfoxide was stirred as a solution of 40.6 g of the crude tosylate in 25 mL of dimethyl sulfoxide was added. The mixture was stirred for 24 h at room temperature, 200 mL of water was added, and the product was extracted with three portions of ether. The combined ether extracts were washed with water and saturated sodium chloride, dried ($MgSO_4$), and evaporated. Distillation of the remaining liquid at reduced pressure through a 5-cm Vigreux column afforded 12.6 g (76% from 3,4-pentadien-1-ol) of the nitrile: bp 78–79 °C (18 mm); IR (film) ν_{max} 2275 (C≡N), 1950 (C=C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.16–2.60 (m, 4 H, 2 CH_2), 4.83 (overlapping d of t, J = 3, 6 Hz, 2 H, CH=C=CH_2), 5.16 (overlapping d of t, J = 6, 12 Hz, 1 H, CH=C=CH_2).

Anal. Calcd for C_6H_7N: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.25; H, 7.70; N, 14.84.

4-Penten-1-yl Trimethylsilyl Ether. A solution of 26.5 g (0.31 mol) of 4-penten-1-ol, 25.0 g (0.15 mol) of hexamethyldisilazane, and 0.25 mL (2.3 mmol) of chlorotrimethylsilane was stirred at 60 °C for 20 h.[17] Two successive distillations at 22–25 mm afforded 46.7 g (95%) of the trimethylsilyl ether as a clear liquid: bp 40–42 °C (22 mm); IR (film) ν_{max} 1640 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H, $OSi(CH_3)_3$), 1.56 (br quintet, J = 7 Hz, 2 H, $CH_2CH_2CH_2$), 2.06 (br q, J = 7 Hz, 2 H, C=CHCH_2), 3.56 (t, J = 6 Hz, 2 H, CH_2OSi), 4.80–5.13 (m, 2 H, CH=CH_2), 5.56–6.03 (10-line m, 1 H, CH=CH_2).

Anal. Calcd for $C_8H_{18}OSi$: C, 60.68; H, 11.48. Found: C, 60.53; H, 11.26.

1,1-Dibromo-2-[3-(trimethylsiloxy)propyl]cyclopropane. A solution of 25.1 g (158 mmol) of 4-penten-1-yl trimethylsilyl ether and 28.0 g (33 mmol) of phenyl(tribromomethyl)mercury in 70 mL of benzene was heated at reflux for 3 h.[18] Phenylmercuric bromide was filtered, and the filter cake was washed 3 times with pentane. The combined filtrates were concentrated by distillation at atmospheric pressure, and the residue was distilled under reduced pressure to give 9.2 g (52% based on phenyl(tribromomethyl)mercury) of the dibromocyclopropane: bp 70–73 °C (0.01 mm); IR (film) ν_{max} 1100 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H, $OSi(CH_3)_3$), 1.10–1.33 (br m, 1 H, cyclopropyl H), 1.33–1.93 (br m, 6 H, 3 CH_2), 3.63 (t, J = 6 Hz, 2 H, CH_2OSi).

Anal. Calcd for $C_9H_{18}OSiBr_2$: C, 32.74; H, 5.51; Br, 48.40. Found: C, 32.82; H, 5.35; Br, 48.45.

4,5-Hexadien-1-yl Trimethylsilyl Ether. A solution of 20.8 g (63 mmol) of 1,1-dibromo-2-[3-(trimethylsiloxy)propyl]cyclopropane in 20 mL of diethyl ether was stirred and cooled at −40 to −45 °C while 105 mL (126 mmol) of a 1.2 M solution of methyllithium in ether was added at a rate such that the internal temperature did not exceed −40 °C. The addition required 40 min. The solution was stirred at −50 °C for 10 min, warmed to 20 °C over 35 min, and cooled again to −40 °C. A 20-mL portion of aqueous sodium bicarbonate was added, and the mixture was allowed to warm to room temperature. The ether layer was separated, and the aqueous layer was extracted 3 times with ether. The combined ether extracts were washed with water, dried ($MgSO_4$), and distilled at atmospheric pressure through a 15.2-cm Vigreux column. Distillation of the residue under reduced pressure furnished 9.1 g (85%) of the allene, bp 71–75 °C (16 mm). A sample was further purified by preparative GLC on column D at 150 °C: IR (film) ν_{max} 1950 (C=C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 9 H, $OSi(CH_3)_3$), 1.63 (br quintet, J = 7 Hz, 2 H, $CH_2CH_2CH_2$), 1.80–2.16 (br m, 2 H, C=CHCH_2), 3.56 (t, J = 6 Hz, 2 H, CH_2OSi), 4.63 (overlapping d of t, J = 3, 6 Hz, 2 H, CH=C=CH_2), 5.06 (overlapping d of t, J = 6, 12 Hz, 1 H, CH=C=CH_2).

Anal. Calcd for $C_9H_{18}OSi$: C, 63.45; H, 10.67. Found: C, 63.80; H, 10.42.

4,5-Hexadien-1-ol. A two-phase mixture of 9.0 g (53 mmol) of 4,5-hexadien-1-yl trimethylsilyl ether in 90 mL of ether and 30 mL of 5% aqueous hydrochloric acid was shaken vigorously in a Paar hydrogenation apparatus at room temperature for 18 h. The aqueous layer was separated, saturated with solid sodium chloride, and extracted with three portions of diethyl ether. The combined ether solutions were washed with saturated sodium bicarbonate and saturated sodium chloride, dried ($MgSO_4$), and

concentrated by distillation through a 15.2-cm Vigreux column at atmospheric pressure. Distillation of the remaining liquid at reduced pressure afforded 4.6 g (81%), bp 75–77 °C (14 mm) [lit.[16] bp 60 °C (2 mm)], of the previously known alcohol.[16] A sample was purified by preparative GLC on column D at 125 °C: IR (film) ν_{max} 2500–3700 (OH), 1950 (C=C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.66 (br quintet, J = 6 Hz, 2 H, $CH_2CH_2CH_2$), 1.86–2.26 (br m, 2 H, C=CH=CH_2), 2.83 (br s, 1 H, OH), 3.60 (t, J = 6 Hz, 2 H, CH_2OH), 4.63 (overlapping d of t, J = 3, 6 Hz, 2 H, CH=C=CH_2), 5.06 (overlapping d of t, J = 6, 12 Hz, 1 H, CH=C=CH_2).

4,5-Hexadienal. A. By Reduction of 4,5-Hexadienenitrile. A solution of 2.0 g (21.4 mmol) of 4,5-hexadienenitrile in 20 mL of dry diethyl ether was stirred and cooled in a dry ice–isopropyl alcohol bath while 4.31 mL (23.6 mmol) of diisobutylaluminium hydride (Texas Alkyls Inc.) as a neat liquid was added at a rate to maintain an internal temperature between −40 and −45 °C. After 30 min at −50 °C, 1 mL of methanol, 30 mL of ether, and 30 g of 2:5 water–silica gel[38] were added. The reaction mixture was stirred for 18 h at room temperature, the silica gel was filtered and washed with ether, and the combined filtrate was dried with sodium bicarbonate and magnesium sulfate. The solvent was removed by distillation at atmospheric pressure through a 15.2-cm Vigreux column. The residual liquid was distilled rapidly into a cooled receiver at a pressure of 8 mm (head temperature, 43 °C) to give 700 mg (34%) of the aldehyde. An analytical sample was obtained by preparative GLC on column C at 150 °C: IR (film) ν_{max} 1950 (C=C=C), 1716 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.10–2.70 (m, 4 H, CH_2CH_2), 4.63 (overlapping d of t, J = 3, 6 Hz, 2 H, CH=C=CH_2), 5.10 (overlapping d of t, J = 6, 12 Hz, 1 H, CH=C=CH_2), 9.70 (s, 1 H, CHO).

Anal. Calcd for C_6H_8O: C, 74.97; H, 8.39. Found: C, 74.54; H, 8.42.

B. By Oxidation of 4,5-Hexadien-1-ol. A literature procedure for the oxidation of alcohols with dimethyl sulfide–*N*-chlorosuccinimide in toluene was modified.[13] A solution of 4.0 g (30 mmol) of *N*-chlorosuccinimide in 125 mL of dichloromethane was stirred and cooled in an ice bath as 3.0 mL (50 mmol) of dimethyl sulfide was added. The aza sulfonium salt precipitated immediately. The supernatant dichloromethane was separated by forcing the solvent with nitrogen pressure through a coarse fritted-glass filter tube immersed in the mixture and replaced with 70 mL pentane. The pentane suspension was stirred and cooled at −25 °C as 1.95 g (20 mmol) of 4,5-hexadien-1-ol was added. The mixture was stirred for 2 h at −25 °C, 3.0 g (30 mmol) of triethylamine was added, and the cooling bath was removed. The pentane suspension was stirred for another 20 min, the salts remaining in the flask were washed 3 times with pentane, the pentane washes were filtered over silica gel, and the combined pentane filtrates were washed with saturated copper sulfate and saturated sodium chloride. The pentane solution was dried ($MgSO_4$) and concentrated to 30 mL by distillation at atmospheric pressure through a 15.2-cm Vigreux column. The resulting pentane solution contained 6.4 mmol (32%) of 4,5-hexadienal. The amount of aldehyde in the solution was determined by integration of the aldehyde proton in the NMR spectrum with respect to the aromatic protons of 1,2,4,5-tetramethylbenzene as an internal standard. Another oxidation was performed with 4.6 g (47 mmol) of 4,5-hexadien-1-ol, 9.4 g (70.5 mmol) of *N*-chlorosuccinimide, 7.0 mL (17 mmol) of dimethyl sulfide, and 7.05 g (70 mmol) of triethylamine. The products from the two runs were combined, affording a total of 24 mmol of 4,5-hexadienal in ca. 30 mL of pentane which was used directly for the formation of lactone 7.

3-(3,4-Pentadienyl)-4,5,6,7-tetrahydro-1(3*H*)-isobenzofuranone (7). A. From Bromo Amide 6. A solution of 8.5 g (36 mmol) of bromo amide 6[12] in 70 mL of THF was stirred and cooled at −85 °C as 40 mL (80 mmol) of 2 M *tert*-butyllithium in pentane was added dropwise at a rate to maintain an internal temperature between −75 and −80 °C. The solution was stirred for 45 min at −85 °C, and 1.2 g (9 mmol) of *tert*-butyl bromide was added to destroy excess *tert*-butyllithium.[11] A solution of 24 mmol of 4,5-hexadienal in 30 mL of pentane was slowly added, keeping the internal temperature below −65 °C. The resulting solution was stirred for 10 min at −75 to −85 °C, 10 mL of 1:1 20% aqueous acetic acid–THF was added, and the temperature was raised to 0 °C. Saturated sodium chloride solution and solid sodium chloride were added, and the aqueous layer was extracted 3 times with ether. The combined extracts were washed with 10% aqueous hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride. The ethereal solution was dried ($MgSO_4$) and evaporated to yield 8.0 g of a yellow oil. The product was purified by chromatography on a 350-g column of silica gel, using 1:4 diethyl ether–hexane as eluent and collecting 25-mL fractions. Fractions 74–151 gave, after evaporation of the solvent, 4.6 g (96% based on 4,5-hexadienal) of lactone 7. An analytical sample was prepared by Kughelrohr distillation (0.03 mm) at an oven temperature of 145–155 °C: IR (film) ν_{max} 1961 (C=C=C), 1748 (lactone C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33–1.96 (br m, 6 H, 3 CH_2), 2.00–2.40 (br m, 6 H, 3 allylic CH_2), 4.63 (quintet, J = 3 Hz, 2 H, CH=C=CH_2), 4.70 (br d overlapping with quintet, 1 H, C=CCHOR), 5.10 (overlapping d of t, J = 6, 12 Hz, 1 H, CH=C=CH_2).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.43; H, 8.03.

B. From Ester 12a. The procedure of Miyashita and coworkers was used for the removal of the tetrahydropyranyl ether protecting group.[25] A solution of 50 mg (0.156 mmol) of ester **12a** and 5.9 mg (0.023 mmol) of pyridinium *p*-toluenesulfonate in 1.5 mL of absolute ethanol was stirred at 55 °C for 5 h. The solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on a 10-mm column with 3:7 ethyl acetate–hexane as eluant, affording 24 mg (75%) of lactone 7 as a colorless oil. The IR and NMR spectra of 7 are identical with those obtained from the product in part A above.

2,5-Dichloro-2-pentene. 2,5-Dichloro-2-pentene was prepared by the method of Demmon and Lansbury.[39] Cyclopropyl methyl ketone (25.00 g, 0.30 mol) was added to 70.7 g (0.34 mol) of solid phosphorus pentachloride with rapid mechanical stirring over a 45-min period. A water bath was used to cool the mixture during the addition period. Stirring was continued at room temperature for 1 h, and the mixture was then warmed to 100 °C for 5.5 h. The yellow solution was cooled to room temperature, stirred for 12 h, and poured onto ice. After 1.5 h, the mixture was extracted with several portions of ether. The combined ethereal extracts were washed with water, saturated sodium bicarbonate, and saturated sodium chloride before drying ($MgSO_4$). The solvent was evaporated by distillation at atmospheric pressure through a 15-cm column packed with glass helices. Distillation of the residue through the same column furnished 20.89 g (50%) of 2,5-dichloro-2-pentene as a colorless liquid: bp 74–80 °C (60 mm) [lit.[40] bp 48–52 °C (14 mm)]. A GLC analysis of the product (column A; temperature program, 155 °C, 20 °C/min to 240 °C) indicated an isomer ratio of 60% *E* and 40% *Z*.[40] The NMR spectral properties for the dichloride agree with the literature data.[40]

2-Chloro-5-iodo-2-pentene. The procedure of Kreiser and Janitschke[21] was employed with some modifications. A mixture of 20.89 g (0.150 mol) of 2,5-dichloro-2-pentene and 112.5 (0.750 mol) of finely powdered sodium iodide in 350 mL of acetone was stirred at reflux in the dark for 12 h. The solvent was evaporated, and about 200 mL of 1:1 ether–water was added to the residue. The aqueous layer was extracted with several portions of ether. The combined organic extracts were washed with saturated sodium chloride, dried ($MgSO_4$), and filtered through a pad of neutral alumina. Evaporation of the solvent and distillation of the residue through a 15-cm Vigreux column gave the iodide as a dark-red liquid, bp 78–87 °C, which was decolorized by filtration through a short pad of neutral alumina: yield, 25.64 g (75%). A GLC analysis of the product on column B (temperature program, 50 °C 3 min, 20 °C/min increased to 200 °C) indicated an *E*/*Z* isomer ratio of 3:1. The ^{1}H NMR spectral data for the mixture correspond to those in the literature.[21]

1-(2-Bromo-1-cyclohexenyl)-5-chloro-4-hexen-1-ol (8). (4-Chloro-3-pentenyl)lithium was generated by the procedure of

(38) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63–65.

(39) Demmin, T. R. Ph.D. Dissertation, The State University of New York, Buffalo, NY, 1972. This procedure was kindly provided by Professor Peter Lansbury.

(40) Newman, M. S.; Kaugars, G. *J. Org. Chem.* **1966**, *31*, 1379–83.

Lansbury and co-workers.[20] A solution of 10.51 g (45.62 mmol) of 2-chloro-5-iodo-2-pentene in 75 mL of sodium-dried ether was stirred at −78 °C, and 31 mL (73.79 mmol) of 2.38 M *tert*-butyllithium in pentane was added over 15 min. Stirring was continued for 5 min at −78 °C. A solution of 6.34 g (33.54 mmol) of bromo aldehyde **1** in 10 mL of ether was added via a pressure-equalized addition funnel over 5 min, and the funnel was washed with three 10-mL portions of ether. The solution was warmed to room temperature and hydrolyzed with 25 mL of saturated sodium chloride. The aqueous layer was extracted with two 50-mL portions of ether. The combined organic extracts were washed with saturated sodium chloride, dried ($MgSO_4$), and evaporated. Purification of the residue by flash chromatography on a 60-mm column with 1:4 ethyl acetate–hexane as eluant gave 8.36 g (85%) of bromo alcohol **8** as a pale-yellow oil. GLC analysis of the product on column A (temperature program, 150 °C, 20 °C/min to 300 °C) indicated an isomer ratio of 3:1. The spectral properties of **8** are as follows: IR (film) ν_{max} 3300 (OH), 2810 (C=CH), 1650 (C=C), 1645 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38–1.85 (m, 6 H, 3 CH_2), 1.90–2.15 (4-line m, ~3 H, C=CCH_3), 1.90–2.33 (m, 5 H, 2 allylic CH_2, OH), 2.33–2.62 (m, 2 H, allylic CH_2), 4.73 (t, J = 7 Hz, 1 H, CHOH), 5.33–5.72 (m, 1 H, C=CH); high-resolution mass spectrum calcd for $C_{12}H_{18}BrClO$ m/e 292.0225 (M^+), found m/e 292.0220.

3-(4-Chloro-3-pentenyl)-4,5,6,7-tetrahydro-1(3*H*)-isobenzofuranone (9). A solution of 250 mg (0.85 mmol) of bromo alcohol **8** in 2.5 mL of anhydrous tetrahydrofuran was cooled to −90 °C and stirred while 1.25 mL (2.98 mmol) of 2.38 M *tert*-butyllithium in pentane was added over 5 min. The solution was warmed to −45 °C over 10 min, stirred at this temperature for 1 h, and then transferred via a double-pointed cannula to a vigorously stirred solution of excess anhydrous carbon dioxide in 5 mL of tetrahydrofuran at −78 °C. The solution was warmed to room temperature and poured into 15 mL of 5% hydrochloric acid. The aqueous layer was extracted with several portions of ether. The combined organic solutions were washed with saturated sodium bicarbonate and saturated sodium chloride, dried ($MgSO_4$), and evaporated. Purification of the product by flash chromatography on a 20-mm column with 1:4 ethyl acetate–hexane as eluant afforded 116 mg (57%) of lactone **9** as a colorless oil. A GLC analysis of the product on column A (temperature program, 160 °C, 20 °C/min to 300 °C) indicated an isomer ratio of 2.4:1. The spectral data for the isomer mixture are as follows: IR (film) ν_{max} 2850 (C=CH), 1750 (C=O), 1675 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–2.00 (m, 6 H, 3 CH_2), 2.03–2.12 (4-line m, ~3 H, C=CCH_3), 2.03–2.50 (m, 5 H, 5 allylic CH), 2.53–2.82 (m, 1 H, allylic CH), 4.66–4.93 (br m, $W_{1/2}$ = 18 Hz, 1 H, CHOR), 5.52 (q, J = 7 Hz, 1 H, C=CH); high-resolution mass spectrum calcd for $C_{13}H_{17}ClO_2$ m/e 240.0913 (M^+), found m/e 240.0916.

5-Bromo-1,2-pentadiene.[41] A solution of 21.30 g (0.254 mol) of 3,4-pentadien-1-ol[41,42] and 39.2 g (0.387 mol) of triethylamine (freshly distilled from calcium hydride) in 350 mL of dichloromethane was stirred and cooled in an ice bath as 31.8 g (0.278 mol) of methanesulfonyl chloride was added dropwise over 1 h. Stirring was continued for 3 h after which 300 mL of ice–water was added to hydrolyze any remaining sulfonyl chloride. The aqueous layer was extracted once with dichloromethane, and the combined organic layers were washed twice with 5% hydrochloric acid, twice with saturated sodium bicarbonate, and once with saturated sodium chloride. The solution was dried (Na_2SO_4/K_2CO_3) and the solvent was removed on a rotary evaporator at 25 °C. The crude methanesulfonate (40.63 g, 99%) was used without purification.

A suspension of 50 g (0.575 mol) of anhydrous lithium bromide in 220 mL of acetone was stirred at room temperature as 20 g (0.123 mol) of the crude methanesulfonate was added. After 18 h, 160 mL of water was added and the aqueous mixture was extracted once with ether. The organic phase was washed 3 times with water, dried, and concentrated. Distillation through a 10-cm Vigreux column afforded 13.22 g (73%) of 5-bromo-1,2-pentadiene: bp 75–77 °C (110 mm) [lit.[43] bp 69–70 °C (70 mm)]; ^1H NMR ($CDCl_3$) δ 2.55 (9-peak m, 2 H, allylic CH_2), 3.43 (t, 2 H, J = 7.5 Hz, CH_2Br), 4.75 (quintet, 2 H, J = 3 Hz, =CH_2), 5.13 (quintet, 1 H, J = 7 Hz, =CH).

1-(2-Bromo-1-cyclohexenyl)-4,5-hexadien-1-ol (10). A mixture of 0.88 g (36.26 mmol) of magnesium turnings and 7.01 g (37.33 mmol) of 1,2-dibromoethane in 100 mL of anhydrous tetrahydrofuran was stirred and heated at reflux under an atmosphere of dry argon.[22] After 1 h, the mixture was cooled to room temperature, and 2.66 g (68.01 mmol) of potassium metal was added. The mixture was stirred vigorously and heated at reflux for 2.5 h. The resulting suspension of highly reactive magnesium was cooled to −85 °C and stirred as 4.78 g (32.52 mmol) of 5-bromo-1,2-pentadiene was added. Stirring was continued for 30 min to complete the formation of the Grignard reagent, after which 2.25 g (11.89 mmol) of bromo aldehyde **1** was added via syringe. The syringe was rinsed with three 3-mL portions of tetrahydrofuran, and the reaction mixture was warmed to room temperature. Saturated ammonium chloride was added, and the aqueous layer was extracted with several portions of ether. The organic extract was washed with saturated sodium chloride, dried ($MgSO_4$), and evaporated. Purification of the residue by flash chromatography on a 30-mm column with 1:4 ethyl acetate–hexane as eluant afforded 2.07 g (68%) of the bromo alcohol (**10**) as a light-yellow oil, which solidified on standing. Recrystallization from pentane gave a white crystalline solid: mp 49–50 °C; IR (film) ν_{max} 3300 (OH), 1950 (C=C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–1.81 (m, 7 H, 3 CH_2 and OH), 1.81–2.32 (m, 4 H, 2 allylic CH_2), 2.32–2.64 (m, 2 H, allylic CH_2), 4.54–4.90 (m, 3 H, CH=CCH_2, CHOH), 4.94–5.30 (q, J = 6 Hz, 1 H, C**H**=C=CH_2).

Anal. Calcd for $C_{12}H_{17}BrO$: C, 56.03; H, 6.68; Br, 31.07. Found: C, 55.89; H, 6.79; Br, 31.03.

6-(2-Bromo-1-cyclohexenyl)-6-(tetrahydropyran-2-yloxy)-1,2-hexadiene (11a). The procedure of Miyashita and co-workers were employed for the protection of alcohol **10**.[25] A solution of 322 mg (1.25 mmol) of bromo alcohol **10**, 218 mg (2.50 mmol) of dihydropyran, and 31.4 mg (0.125 mmol) of pyridinium *p*-toluenesulfonate in 10 mL of anhydrous dichloromethane was stirred at room temperature. After 4 h, 20 mL of saturated sodium bicarbonate was added, and the aqueous layer was extracted with two portions of ether. The organic extracts were washed with saturated sodium chloride, dried ($MgSO_4$), and evaporated. Purification of the residue by flash chromatography on a 20-mm column with 1:4 ethyl acetate–hexane as eluant afforded 407 mg (95%) of tetrahydropyranyl ether **11a** as a light-yellow oil: IR (film) ν_{max} 1960 (C=C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30–1.90 (m, 12 H, 6 CH_2), 1.85–2.20 (m, 4 H, 2 allylic CH_2), 2.35–2.65 (m, 2 H, allylic CH_2), 3.34–4.05 (m, 2 H, CH_2OR), 4.30–5.00 (m, 4 H, CH=CCH_2, C=CHOR, ROCHOR), 5.00–5.30 (m, 1 H, C**H**=C=CH_2).

Anal. Calcd for $C_{17}H_{25}BrO_2$: C, 59.82; H, 7.40; Br, 23.41. Found: C, 60.23; H, 7.40; Br, 23.63.

6-(2-Bromo-1-cyclohexenyl)-6-[(2-methoxyethoxy)methoxy]-1,2-hexadiene (11b). The procedure of Corey and co-workers[24] was used for the protection of alcohol **10**. A solution of 300 mg (1.17 mmol) of bromo alcohol **10**, 220 mg (1.76 mmol) of (β-methoxyethoxy)methyl chloride, and 227 mg (1.76 mmol) of diisopropylethylamine in 8 mL of dichloromethane was stirred for 13 h at room temperature. The solution was diluted with ether, extracted with saturated sodium chloride, dried (Na_2SO_4), and evaporated. Purification by flash chromatography on a 20-mm column with 1:4 ethyl acetate–hexane as eluant afforded 366 mg (91%) of (methoxyethoxy)methyl ether **11b** as a light-yellow oil: IR (film) ν_{max} 1950 (C=C=C), 1655 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54–1.85 (m, 6 H, 3 CH_2), 1.85–2.32 (m, 4 H, 2 allylic CH_2), 2.33–2.65 (m, 2 H, allylic CH_2), 3.37 (s, 3 H, OCH_3), 3.45–3.82 (m, 4 H, OCH_2CH_2O), 4.56–4.87 (m, 3 H, CH=C=CH_2, CHOR), 4.60 (s, ~2 H, OCH_2O), 5.00–5.29 (q, 1 H, J = 7 Hz, C**H**=C=CH_2).

Anal. Calcd for $C_{16}H_{25}BrO_3$: C, 55.65; H, 7.31; Br, 23.14. Found: C, 55.87; H, 7.31; Br, 23.00.

Methyl 2-[1-(Tetrahydropyran-2-yloxy)-4,5-hexadien-1-yl]-1-cyclohexenecarboxylate (12a). A solution of 93 mg (0.273 mmol) of vinyl bromide **11a** in 4 mL of tetrahydrofuran was cooled

(41) This compound was prepared by Jack W. Muskopf to whom we are grateful.

(42) Olsson, L. I.; Claesson, A.; Bogentoft, C. *Acta Chem. Scand., Ser. B* **1974**, *28*, 765–70.

(43) Black, D. K.; Landor, S. R.; Patel, A. N.; Whiter, P. F. *J. Chem. Soc. C* **1967**, 2260–2262.

to −100 °C and stirred while 0.46 mL (0.819 mmol) of 1.79 M *tert*-butyllithium in pentane was added over 12 min. The solution was warmed to −80 °C over 2 min and excess anhydrous solid carbon dioxide was added. The solution was warmed to room temperature, diluted with 50 mL of ether, and extracted with three portions of 10% sodium carbonate. The combined aqueous layers were acidified with ice-cold concentrated hydrochloric acid, saturated with sodium chloride, and extracted with three 20-mL portions of ether. The organic extracts were washed with saturated sodium chloride and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure furnished the crude acid, which was esterified at 0 °C with excess diazomethane in ether. Evaporation of the solvent and purification of the residue by flash chromatography on a 10-mm column with 1:4 ethyl acetate–hexane as eluant afforded 43 mg (49%) of allene ester **12a** as a colorless oil: IR (film) ν_{max} 2870 (C=CH), 1960 (C=C=C), 1655 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35–1.89 (m, 12 H, 6 CH_2), 1.89–2.60 (m, 6 H, 3 allylic CH_2), 3.25–4.05 (m, 2 H, CH_2OR), 3.78 (s, 3 H, $COOCH_3$), 4.35–5.00 (m, 4 H, CH=C=CH_2, CCHOR, ROCHOR), 5.00–5.30 (m, 1 H, CH=C=CH_2).

Methyl 2-[1-((2-Methoxyethoxy)methoxy)-4,5-hexadien-1-yl]-1-cyclohexenecarboxylate (12b). A solution of 1.00 g (2.90 mmol) of vinyl bromide **11b** in 100 mL of tetrahydrofuran was cooled to −90 °C and stirred while 4.03 mL (7.25 mmol) of 1.80 M *tert*-butyllithium in pentane was added over a 1-min period. After 2 min, excess anhydrous solid carbon dioxide was added. The solution was warmed to room temperature, diluted with ether, and extracted with several portions of 10% sodium carbonate. The combined aqueous layers were acidified with ice-cold concentrated hydrochloric acid, saturated with sodium chloride, and extracted with several portions of ether. The organic extracts were washed with saturated sodium chloride, dried ($MgSO_4$), and evaporated. A solution of the crude acid in ether was esterified with diazomethane at 0 °C. Evaporation of the solvent and purification of the residue by flash chromatography on a 30-mm column with 3:7 ethyl acetate–hexane as eluant afforded 614 mg (65%) of allene ester **12b** as a pale-yellow oil: IR (film) ν_{max} 1950 (C=C=C), 1715 (C=O), 1630 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43–1.83 (m, 6 H, 3 CH_2), 1.85–2.40 (m, 6 H, 3 allylic CH_2), 3.37 (s, 3 H, OCH_3), 3.43–3.80 (m, 4 H, OCH_2CH_2O), 3.70 (s, ~3 H, $COOCH_3$), 4.50–5.22 (m, 4 H, CH=C=CH_2, CHOR), 4.58 (s, 2 H, OCH_2O).

Anal. Calcd for $C_{18}H_{28}O_5$: C, 66.63; H, 8.72. Found: C, 66.26; H, 8.61.

2-Hydroxytricyclo[5.4.0.0^{1,5}]undecane-7-carboxylic Acid Lactone (13). A solution of 1.9 g (9.9 mmol) of lactone **4** in 200 mL of reagent grade acetone was placed in an irradiation vessel fitted with a quartz immersion well. Dry nitrogen was bubbled through the solution to remove dissolved oxygen. The solution was stirred and irradiated for 65 min with a 450-W medium-pressure Hanovia lamp placed inside a 1-mm thick cylindrical Vycor sleeve. The solvent was removed by rotary evaporation to give 2.1 g of crude lactone **13**. Purification by MPLC on 70 g of silica gel, using 1:2 diethyl ether–hexane, gave 1.4 g (77%) of lactone **13**: IR (film) ν_{max} 1750 (lactone C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.50 (br m, 15 H, 7 CH_2 and CH), 4.50 (ca. d of d, J = 2 Hz, 1 H, CHOH).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.78; H, 8.67.

2-Hydroxy-6-methyltricyclo[5.4.0.0^{1,5}]undecane-7-carboxylic Acid Lactone (14). A solution of 500 mg (2.43 mmol) of lactone **5** in 20 mL of acetone was degassed with nitrogen and irradiated for 20 min in a one-piece, cylindrical, quartz apparatus having an inner cooling jacket and an outer solution jacket as described above. Purification by flash chromatography on a 20-mm column with 3:7 ethyl acetate–hexane as eluant afforded 310 mg (66%) of **14** as a colorless oil. GLC analysis of the product on column A (temperature program, 160 °C, 20 °C/min to 250 °C) indicated an isomer ratio of 1:1.6: IR (film) ν_{max} 1760 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (d, J = 8 Hz, $CHCH_3$), 1.20 (d, J = 8 Hz, $CHCH_3$), 0.90–2.80 (m, 17 H), 4.42–4.63 (m, 1 H, CHOR).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.68; H, 8.81. Found: C, 75.93; H, 8.72.

6-Chloro-2-hydroxy-6-methyltricyclo[5.4.0.0^{1,5}]undecane-7-carboxylic Acid Lactone (15). A solution of 288 mg (1.200 mmol) of lactone **9** in 15 mL of benzene was irradiated for 8 h in a one-piece quartz apparatus as described for the irradiation at lactone **5**. The solvent was evaporated, and the dark-green residue was purified by flash chroamtography on a 20-mm column with 1:4 ethyl acetate–hexane as eluant, affording 99 mg (34%) of **15** as a light-yellow solid. Recrystallization from pentane gave fine white needles: mp 88–91 °C; IR ($CDCl_3$) ν_{max} 1755 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35–2.38 (m, 12 H), 1.51 (s, 3 H, CH_3), 2.63–2.87 (m, 1 H), 4.46 (d, J = 2 Hz, 1 H, CHOR).

Anal. Calcd for $C_{13}H_{17}ClO_2$: C, 64.85; H, 7.13; Cl, 14.72. Found: C, 64.69; H, 7.30; Cl, 14.72.

2-Hydroxy-11-methylenetricyclo[5.4.0.0^{1,5}]undecane-7-carboxylic Acid Lactone (17), 10-Hydroxy-11-methylenetricyclo[5.3.1.0^{1,6}]undecane-6-carboxylic Acid lactone (18), and 2-Hydroxytricyclo[6.4.0.0^{1,6}]dodec-5-ene-8-carboxylic Acid Lactone (19). A solution of 1.200 g (5.88 mmol) of allene lactone **7** in 200 mL of degassed *p*-xylene was stirred and irradiated for 2.5 h with a 450-W medium-pressure Hanovia lamp in a quartz immersion well apparatus. The solvent was evaporated under reduced pressure, and the residue was purified by medium-pressure liquid chromatography, using 1:9 ether–hexane as eluant. The first photoproduct to be eluted from the column was lactone **18** which was obtained as colorless oil: yield, 188 mg (16%); IR (film) ν_{max} 1770 (C=O), 1667 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–2.30 (m, 12 H, 6 CH_2), 2.82 (br s, $W_{1/2}$ = 8 Hz, 1 H, allylic CH), 4.51 (br s, $W_{1/2}$ = 5 Hz, 1 H, CHOR), 4.90 (s, 1 H, C=CH), 4.98 (s, 1 H, C=CH).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.34; H, 7.98.

Lactone **17** eluted second and was obtained as a colorless oil: yield, 395 mg (33%). Recrystallization from pentane gave a white solid: mp 63–64 °C; IR (film) ν_{max} 1764 (lactone C=O), 1681 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.76 (m, 6 H, 3 CH_2), 1.76–2.43 (m, 6 H, 3 CH_2), 2.95–3.23 (m, 1 H, C=CH), 4.77 (t, J = 2 Hz, 1 H, CHOR), 5.13 (m, 1 H, C=CH), 5.30 (m, 1 H, C=CH).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.25; H, 8.02.

Lactone **19** was eluted next and was recrystallized from pentane, giving fine white needles: yield, 85 mg (7%); mp 80–81 °C; IR (film) ν_{max} 2850 (C=CH), 1770 (C=O) cm^{-1}; 220-MHz ^1H NMR ($CDCl_3$) δ 1.00–1.18 (m, 1 H, CH), 1.31–1.44 (m, 3 H, 3 CH), 1.60–1.85 (m, 6 H, 3 CH_2), 1.93 (dd, J = 2, 7 Hz, 1 H, CH), 2.08–2.19 (m, 2 H, 2 allylic CH), 2.80 (d, J = 12 Hz, 1 H, allylic CH), 3.18 (dd, J = 1.5, 10 Hz, 1 H, allylic CH), 4.37 (d, J = 2 Hz, 1 H, CHOR), 5.58 (d, J = 4 Hz, 1 H, C=CH); mass spectrum (70 eV), m/e 204 (M^+).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.21; H, 7.83.

Dehydrochlorination of Lactone 15. A mixture of 300 mg (1.25 mmol) of lactone **15** and 561 mg (5.00 mmol) of potassium *tert*-butoxide in 5 mL of dry tetrahydrofuran was stirred at room temperature for 20 min. A 10-mL portion of 5% hydrochloric acid was added and the aqueous layer was extracted with three 15-mL portions of ether. The combined ether extracts were washed with saturated sodium carbonate and saturated sodium chloride, dried ($MgSO_4$), and evaporated. Purification of the residue by flash chromatography on a 20-mm column with 1:4 ethyl acetate–hexane as eluant afforded 180 mg (71%) of lactone **17** as a pale-yellow oil. The ^1H NMR spectrum, GLC retention time, and TLC R_f value of the product are the same as those of a sample prepared by irradiation of **7**.

Preparation of Aqueous Sodium Ruthenate Oxidizing Solution. The ruthenium dioxide used for the preparation of sodium ruthenate was purchased as the hydrated form from Engelhard Minerals and Chemical Corp. Attempts to use ruthenium dioxide (hydrated, soluble form) purchased from Alfa Division were unsuccessful.

A 4.90-g portion of ruthenium dioxide hydrate was added to a stirred solution of 13.7 g (64.1 mmol) of sodium metaperiodate in 100 mL of water. The aqueous suspension became opaque yellow within a few minutes. The solution was stirred for 30 min at room temperature and extracted with four 40-mL portions of carbon tetrachloride. The combined organic extracts were mechanically shaken for 30 min with 250 mL of 1 M sodium hydroxide. The dark-orange aqueous layer was washed with two 25-mL portions of carbon tetrachloride and diluted to a final

volume of 400 mL with 1 M sodium hydroxide. The concentration of sodium ruthenate solution was 0.054 M as determined by its UV absorbance at 385 nm (ϵ 1030).[32a]

Recovery of Ruthenium Dioxide. The black ruthenium dioxide deposited during ruthenate oxidations was collected by suction filtration and washed with 5% hydrochloric acid, saturated sodium bicarbonate, water, and methanol. The black paste was air-dried until it became a fine free-flowing powder. The ruthenium dioxide thus obtained was converted to sodium ruthenate in high yield.

2-Oxotricyclo[5.4.0.0^{1,5}]undecane-7-carboxylic Acid (20a). A suspension of 500 mg (2.60 mmol) of lactone **13** in 50 mL of 1 M aqueous sodium hydroxide was warmed on a steam bath for 1 h. The solution was cooled to room temperature and stirred as 55.4 mL (2.86 mmol) of 0.0516 M aqueous sodium ruthenate was added. The solution became very dark, and insoluble material formed immediately. The mixture was stirred for 1 h at room temperature, after which the precipitate was filtered and washed with two portions of water and three portions of ether. The filtrate was acidified with concentrated hydrochloric acid and extracted with three 50-mL portions of ether. The combined organic extracts were washed with two 50-mL portions of saturated sodium chloride, dried ($MgSO_4$), and evaporated, leaving 437 mg of a white solid. Recrystallization of the solid from water–ethanol afforded 268 mg (50%) of keto acid 20a as fine white crystals: mp 157–161 °C. (The product from another similar preparation had mp 154–155 °C); IR ($CHCl_3$) ν_{max} 1736 (C=O), 1701 (carboxylic acid C=O) cm^{-1}; 220-MHz ^{1}H NMR ($CDCl_3$) δ 1.13–2.11 (br m, 10 H, 5 CH_2), 2.13–2.56 (m, 3 H, $COCH_2$, CH), 2.59–2.88 (m, 1 H, CH), 2.88–3.16 (br s, 1 H, CH).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.20; H, 7.76. Found: C, 68.97; H, 7.55.

Methyl 2-Oxotricyclo[5.4.0.0^{1,5}]undecane-7-carboxylate (20b). A solution of 900 mg (4.7 mmol) of crude keto acid **20a**, prepared as described above, in 70 mL of ether was esterified with excess diazomethane in ether for 20 min at room temperature. After excess diazomethane was removed with a stream of nitrogen, the ethereal solution was evaporated, and the crude ester was purified by filtration through ca. 20 g of silica gel with 1:1 ether–hexane as eluent. Evaporation of the filtrate provided 850 mg (81%) of keto ester (**20b**), which crystallized upon refrigeration at −25 °C. The purity of this material was judged to be satisfactory on the basis of its NMR spectrum. An analytical sample was prepared by recrystallization from pentane at 0 °C: mp 60–61 °C; IR ($CHCl_3$) ν_{max} 1724 (C=O) cm^{-1}; 220-MHz ^{1}H NMR ($CDCl_3$) δ 1.22–1.72 (m, 6 H, 3 CH_2), 1.72–1.95 (m, 4 H, 2 CH_2), 2.27–2.50 (m, 3 H, $COCH_2$, CH), 2.68 (overlapping d of t, J = 7, 16 Hz, 1 H, CH), 2.95–3.09 (m, 1 H, CH), 3.68 (s, 3 H, CO_2CH_3).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.23; H, 8.18. Found: C, 70.10; H, 8.09.

6-Methyl-2-oxotricyclo[5.4.0.0^{1,5}]undecane-7-carboxylic Acid (21a). A solution of 4.05 g (19.6 mmol) of lactone **14** in 100 mL of 2 M aqueous sodium hydroxide was heated at reflux for 3 h. The solution was cooled to room temperature and stirred as 230 mL (12.20 mmol) of 0.054 M aqueous sodium ruthenate was added. The mixture was stirred for 2 h at room temperature after which 10 mL of methanol was added to reduce excess ruthenate. The precipitate was collected and washed with two portions of water and three portions of ether. The filtrate was acidified with concentrated hydrochloric acid, saturated with sodium chloride, and extracted with three portions of ether. The combined organic extracts were washed with four 25-mL portions of 1 M sodium hydroxide to remove the acidic products. The combined aqueous layers were acidified with concentrated hydrochloric acid, saturated with sodium chloride, and extracted with four 25-mL portions of ether. The organic extracts were washed with saturated sodium chloride and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure furnished 1.46 g (70%) of acid **21a** as a fine white powder: mp 163–168 °C; IR ($CHCl_3$) ν_{max} 2500–3500 (COOH), 1730 (C=O, cyclopentanone), 1700 (C=O, carboxylic acid) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70–2.25 (m, 11 H), 1.02 (d, J = 7 Hz, ~3 H, $CHCH_3$), 2.25–2.83 (m, 4 H).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.23; H, 8.18. Found: C, 69.96; H, 8.18.

Methyl 6-Methylene-2-oxotricyclo[5.4.0.0^{1,5}]undecane-7-carboxylate (22). A solution of 221 mg (1.08 mmol) of lactone **17** in 10 mL of 1 M aqueous sodium hydroxide was oxidized with 23.1 mL (1.19 mmol) of 0.0516 M aqueous sodium ruthenate as described previously for the preparation of keto acid **20a**. The crude product was esterified with excess diazomethane. Purification by preparative TLC using 2:3 ether–hexane as developing solvent provided 189 mg (75%) of the keto ester (**22**) as a pale-yellow solid. Recrystallization from pentane afforded fine white crystals, mp 45–47 °C: IR (film) ν_{max} 1726 (C=O), 1680 (C=C) cm^{-1}; 220-MHz ^{1}H NMR ($CDCl_3$) δ 1.18–2.13 (m, 9 H), 2.16–2.41 (m, 2 H), 2.70 (8-line m, 1 H), 3.63 (s, 3 H, CO_2CH_3), 5.05 (d, J = 1.8 Hz, 1 H, =CH), 5.14 (d, J = 2.6 Hz, 1 H, =CH). The analytical sample melted at 51–52 °C.

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.59; H, 7.62.

11-Methylene-10-oxotricyclo[5.3.1.0^{1,6}]undecane-6-carboxylic Acid (23). Lactone **18** (63 mg, 0.3 mmol) was hydrolyzed to the hydroxy acid sodium salt in 2 mL of 1 M aqueous sodium hydroxide, and the resulting solution was oxidized with 7 mL (0.34 mmol) of 0.05 M aqueous sodium ruthenate as described previously for lactone **20a**. The product was isolated by the same extraction procedure and obtained as a tan solid (44 mg, 59%). Further purification was effected by recrystallization from water: mp 192–194 °C; IR ($CDCl_3$) ν_{max} 2600–3600 (OH), 1709 (C=O) cm^{-1}; 220-MHz ^{1}H NMR ($CDCl_3$) δ 1.13–2.16 (br m, 8 H, 4 CH_2), 2.16–2.72 (br m, 4 H, $COCH_2$), 3.13 (br s, 1 H, CHOR), 4.95 (s, 1 H, C=CH), 5.13 (s, 1 H, C=CH); high-resolution mass spectrum calcd for $C_{13}H_{16}O_3$ m/e 220.1095 (M$^+$), found m/e 220.1088.

Methyl Decahydro-1-oxo-1*H*-cyclopentacyclooctene-5-carboxylate (24). A solution of 25 mg (3.61 mmol) of lithium in 25 mL of anhydrous ammonia was stirred at reflux temperature while a solution of 150 mg (0.72 mmol) of keto acid **20a** in 2 mL of tetrahydrofuran was added. After 2 min, excess ammonium chloride was added and the ammonia was evaporated. A 20-mL portion of water was added, the pH was adjusted to 4.0 with 5% hydrochloric acid, and the solution was extracted with two 30-mL portions of 1:1 ether–pentane. The combined organic extracts were washed with three 10-mL portions of saturated sodium chloride, filtered through a pad of sodium sulfate, and evaporated. The residue was dissolved in 5 mL of acetone and oxidized with a slight excess of Jones reagent at room temperature for 15 min.[34] Excess oxidant was consumed with isopropyl alcohol. The salts were washed with acetone, and the solvent was evaporated. A solution of the residue in 50 mL of 1:1 ether–pentane was extracted with two 30-mL portions of water and two 20-mL portions of saturated sodium chloride, dried (Na_2SO_4), and evaporated. The crude acid was esterified with excess diazomethane in ether at 0 °C. Evaporation of the solvent and chromatography on 50 g of silica gel with 1:9 ether–hexane as eluant provided 32 mg (20%) of esterified starting material **20b**, and 71 mg (44%) of the ring cleavage product **24** as a colorless oil: IR (film) ν_{max} 1735 (C=O) cm^{-1}; 220-MHz ^{1}H NMR ($CDCl_3$) δ 1.15–1.78 (m, 16 H), 1.92–2.18 (m, 1 H, $CHCOOCH_3$), 3.68 (s, 3 H, $COOCH_3$). GLC analysis of the product (column B; temperature program, 200 °C 4 min, 10 °C/min to 300 °C) revealed three peaks in the ratio 5:3:1. GC–MS analysis of each peak (70 eV), m/e 224 (M$^+$).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.60; H, 9.00. Found: C, 69.66; H, 8.88.

Methyl 6-Methyl-2-oxotricyclo[5.4.0.0^{1,5}]undecane-7-carboxylate (21b) and Methyl Decahydro-4-methyl-1-oxo-1*H*-cyclopentacyclooctene-5-carboxylate (25). A solution of 0.749 g (0.108 mol) of lithium in 500 mL of anhydrous ammonia was stirred at reflux while a solution of 4.78 g (21.5 mmol) of keto acid **21a** in 20 mL of tetrahydrofuran was added over 2 min via syringe. The syringe was washed with two 10-mL portions of tetrahydrofuran. After 8 min, excess lithium was destroyed with 4 mL of 3-hexyne. A 4-mL portion of 1:1 acetic acid–ether solution was added, and the ammonia was evaporated. A suspension of the residue in 250 mL of 10% hydrochloric acid was extracted with four 75-mL portions of ether. The combined organic extracts were washed with saturated sodium chloride, dried by filtration through a pad of sodium sulfate, and evaporated. An ether solution of the crude acid was esterified with excess diazomethane at 0 °C. Evaporation of the solvent and oxidation with excess Jones reagent at 10 °C[34] afforded a mixture of crude keto esters. Excess oxidant was consumed with isopropyl alcohol. The pre-

cipitated chromium salts were washed with acetone, and the solvent was evaporated. A solution of the residue in 100 mL of ether was extracted with saturated sodium bicarbonate and saturated sodium chloride, dried ($MgSO_4$), and evaporated. The crude product was purified by flash chromatography on a 60-mm column with 1:4 ethyl acetate–hexane as eluant. The first product to be eluted from the column was evidently 1:2 mixture of recovered lactone and keto ester **21b** as a pale-yellow oil: yield, 1.30 g (26%); IR (film) ν_{max} 1770 (C=O), 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–2.26 (m, 10 H), 1.00 (d, J = 7 Hz, ~1.8 H, $CHCH_3$), 1.19 (d, J = 7 Hz, ~1.2 H, $CHCH_3$), 2.31–2.85 (m, 4 H), 3.64 (s, 3 H, $COOCH_3$). Keto ester **25** was eluted second and was obtained as a colorless viscous oil. MS (EI) indicated that **25** was contaminated with a small amount of **21b**: yield, 2.82 g (55%); IR (film) ν_{max} 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.71–2.53 (m, 14 H), 0.90 (d, J = 6 Hz, ~1.2 H, $CHCH_3$), 0.95 (d, J = 6 Hz, ~1.8 H, $CHCH_3$), 3.64 (s, 3 H, $COOCH_3$); high-resolution mass spectrum calcd for $C_{14}H_{22}O_3$ m/e 238.1563 (M^+), found m/e 238.1564.

Methyl 2,3,3a,6,7,8,9,9a-Octahydro-4-methyl-1-oxo-1*H*-cyclopentacyclooctene-5-carboxylate (26). A refluxing solution of 4.6 mg (0.67 mmol) of lithium in 20 mL of anhydrous ammonia was stirred while 36 mg (0.15 mmol) of keto ester **22** in 2 mL of tetrahydrofuran was added over a 2-min period. After 5 min, excess lithium was destroyed with 0.05 mL of 3-hexyne. A 1-mL portion of 1:1 acetic acid-tetrahydrofuran solution was added, and the ammonia was evaporated. A solution of the residue in 30 mL of 1:1 ether–pentane was extracted with 25 mL of water and two 20-mL portions of saturated sodium chloride and was filtered through a pad of sodium sulfate. Evaporation of the solvent left 42 mg of isomeric keto esters as an oily yellow solid.

The crude product from the reduction was dissolved in 10 mL of a freshly prepared solution of 0.1 M sodium methoxide in methanol. The solution was heated at reflux for 19 h. At periodic intervals, 5-μL aliquots were removed and added to 20 μL of a 1:1 mixture of 5% hydrochloric acid–ether. The course of equilibration could be monitored by GLC analysis (column A; temperature program, 210 °C 3 min, 5 °C/min to 300 °C). After 19 h, only one peak was observed. The solution was cooled, diluted with 40 mL of saturated sodium chloride, and extracted with 30 mL of 1:1 ether–pentane. The organic layer was washed with 20 mL of saturated sodium chloride, filtered through a pad of sodium sulfate, and concentrated. Purification of the residue by preparative TLC, using 1:1 ether–hexane as eluant, gave 26 mg (72%) of keto ester **26** as a pale-yellow solid. An analytical sample was obtained by recrystallization from pentane: mp 72–73 °C; IR ($CHCl_3$) ν_{max} 1730 (C=O), 1709 (ester C=O) cm^{-1}; 220-MHz ^1H NMR ($CDCl_3$) δ 1.23–1.36 (m, 2 H, CH_2), 1.73–2.36 (m, 7 H, ring CH), 2.03 (s, ~3 H, $C=CCH_3$), 2.36–3.05 (m, 4 H, 3 allylic CH and ring CH), 3.59–3.91 (8-line m, 1 H, COCH), 3.74 (s, 3 H, $COOCH_3$); UV (hexane) λ_{max} 230 nm (ϵ 7380); high-resolution mass spectrum calcd for $C_{14}H_{20}O_3$ m/e 236.1407 (M^+), found m/e 236.1412.

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Registry No. 1, 38127-47-8; **2**, 82430-72-6; (*E*)-**3**, 82430-73-7; **4**, 76379-96-9; (*E*)-**5**, 82430-74-8; **6**, 68965-63-9; **7**, 76379-97-0; (*E*)-**8**, 82430-75-9; (*E*)-**9**, 82430-76-0; **10**, 82430-77-1; **11a**, 82430-78-2; **11b**, 82430-79-3; **12a**, 82430-80-6; **12b**, 82430-81-7; **13**, 76379-98-1; **13** hydroxy acid sodium salt, 82430-90-8; **13** keto acid sodium salt, 82430-93-1; **14**, 82430-82-8; **15**, 82430-83-9; **17**, 76379-99-2; **17** hydroxy acid sodium salt, 82430-91-9; **17** keto acid sodium salt, 82430-94-2; **18**, 76380-00-2; **18** hydroxy acid sodium salt, 82430-92-0; **19**, 82430-84-0; **20a**, 76380-01-3; **20b**, 76380-02-4; **21a**, 82430-85-1; **21b**, 82430-86-2; **22**, 76380-03-5; **23**, 76380-06-8; **24**, 76380-04-6; **25**, 82430-87-3; **26**, 76380-05-7; cyclohexanone, 108-94-1; 4-bromo-1-butene, 5162-44-7; (*E*)-5-bromo-2-pentene, 7515-62-0; cyclopropyl methyl ketone, 765-43-5; cyclopropyl methyl carbinal, 765-42-4; 4-penten-1-ol, 821-09-0; 4-pentenal, 2100-17-6; 2-penten-4-yn-1-ol, 5557-88-0; 3,4-pentadien-1-ol, 24767-71-3; 3,4-pentadien-1-ol tosylate, 5557-87-9; 4,5-hexadienenitrile, 82430-88-4; 4-penten-1-yl trimethylsilyl ether, 14031-96-0; phenyl(tribromomethyl)mercury, 3294-60-8; 1,1-dibromo-2-[3-(trimethylsiloxy)propyl]cyclopropane, 82430-89-5; 4,5-hexadien-1-yl trimethylsilyl ether, 72038-66-5; 4,5-hexadien-1-ol, 40365-64-8; 4,5-hexadienal, 20521-51-1; (*E*)-2,5-dichloro-2-pentene, 5680-46-6; (*Z*)-2,5-dichloro-2-pentene, 5680-47-7; (*E*)-2-chloro-5-iodo-2-pentene, 70048-60-1; 3,4-pentadien-1-ol methanesulfonate, 82444-37-9; 5-bromo-1,2-pentadiene, 5558-05-4.

Structure of Physoperuvine

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Evidence, chemical and spectroscopic in character, is presented that suggests that the structure 3-(methylamino)cycloheptanone (1) assigned to the alkaloid physoperuvine by earlier investigators may have to be revised.

The roots of *Physalis peruviana* (Solanaceae) contain the alkaloidal base physoperuvine as both the optically active (crystalline) and the racemic (liquid) variety, isolated by Ray and co-workers.[1,2] Chemical and spectroscopic investigations by these workers have led them to formulate the compound as 3-(methylamino)cycloheptanone (1, Chart I).

A critical examination of the chemical and spectroscopic observations detailed in these papers, coupled with our own studies in this area, force us to the conclusion that this formulation must be revised.

We are puzzled by a number of observations in these publications. For example, the carbonyl band in the IR spectrum of the alkaloid (at 1698 cm^{-1}) is described as weak.[1] We have synthesized several (methylamino)- and (dimethylamino)cycloalkanones, and in all cases we find the carbonyl band is very intense—the most intense band in the spectrum. There do not seem to be any structural features in 1 that would lead one to anticipate weak carbonyl absorption, and, indeed, synthetic 1 (see below) does exhibit a very intense absorption in the carbonyl region. Next, (+)-physoperuvine is described as a crystalline base of mp 153 °C.[1,2] "Chemical intuition" suggested to us that this melting point is unusually high for the structurally simple compound 3-(methylamino)cycloheptanone. Further, the mass spectral fragmentation diagram[1] will not lead to the ion formulated, and the ^{13}C NMR spectrum[2] of *N*-benzoylphysoperuvine (formulated as **2**) is not in agreement with that anticipated for **2**. For example, the chemical shift of the methyl group in **2** would be expected to be around δ 30–35 rather than 55.9. Cases for com-

(1) Ray, A. B.; Sahai, M.; Sethi, P. D. *Chem. Ind. (London)* **1976**, 454.
(2) Sahai, M.; Ray, A. B. *J. Org. Chem.* **1980**, *45*, 3265.

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