acid 13 which was decarboxylated without further purification.

The crude acid 13 was a mixture of two components: TLC (ethanol) R_f 0.57 (major), 0.88 (minor). Both components dissolved in 5% aqueous sodium bicarbonate and reappeared in the organic extract after acidification with hydrochloric acid: IR ($CHCl_3$) 3680, 3618 (both sharp), 3450 (br), 1740 (br), 1630 cm^{-1}; ^1H NMR (60 MHz) δ 7.07 (br s, D_2O labile, COOH[21]), 6.63 (m, H-13), 6.23 (d, H-14, $J_{14,13}$ = 16 Hz), 5.15 (m, H-9), 4.3–2.2 (m, remaining H), 2.07 (s, $OCOCH_3$), 1.30 (m, H-18, 19), 0.92 (m, H-20).

Decarboxylation of 13. A solution of crude carboxylic acid 13 (168 mg, 0.46 mmol) in 100 mL of glacial acetic acid was refluxed for 3.5 h and then concentrated to a brown gum. This was dissolved in 10 mL of methylene chloride and filtered through a 2.5-cm column of silica in a sintered-glass funnel. The silica was washed with 100 mL each of methylene chloride and ethyl acetate, which were combined with the original organic filtrate and concentrated to 115.3 mg (78%) of a colorless, viscous oil which showed one spot on TLC (1/1 ethyl acetate/hexane), R_f 0.52, and one peak on HPLC T_r (I) = 7.3 min. IR and NMR spectra of this enone (8a) were identical with those of the sample prepared above, and the two samples were indistinguishable on HPLC (I).

(21) There are several examples of such uncharacteristic carboxyl group chemical shifts, due to intramolecular hydrogen bonding perhaps: C. J. Pouchert and J. R. Campbell, Eds., "The Aldrich Library of NMR Spectra", Aldrich Chemical Co., Milwaukee, WI, 1974. Vol. 2, Spectra No. 174B (δ 6.0), 171C (δ 7.3), 171B (δ 8.3), 170A (δ 8.5).

Acknowledgment. We are especially grateful to Dr. John Blount of Hoffman La Roche for the X-ray structures he so kindly provided, to Dr. William Schreiber (IFF) and Dr. Vaskin Paragamian (McNeil Labs) for large-scale extractions of Coprosma plants. Dr. James Bobbitt (University of Connecticut, Storrs, CT) and Dr. Victor Plouvier (Museum of Natural History, Paris, France) graciously provided us with generous samples of asperuloside which were of great assistance at the beginning of our work. This work was supported by grants from the CUNY (11088) and the NIH (GM 22098), for which we give thanks.

Registry No. 3, 18842-95-0; 4, 80447-72-9; 5, 80447-73-0; 6, 80447-74-1; 7a, 80447-75-2; 8a, 78323-84-9; 9, 80482-91-3; 10, 78323-80-5; 11, 78323-81-6; 12 (isomer 1), 78323-82-7; 12 (isomer 2), 78342-14-0; 13, 78323-83-8.

Supplementary Material Available: Lists of atomic parameters, bond lengths, and bond angles and a diagram of the structure (4 pages). Ordering information is given on any current masthead page.

Copper(I) Catalysis of Olefin Photoreactions. 10. Synthesis of Multicyclic Carbon Networks by Photobicyclization

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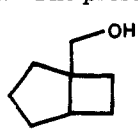
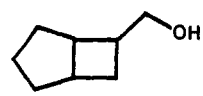
Received September 14, 1981

The synthetic utility of copper-catalyzed photobicyclization for construction of tricyclic ring systems is explored. UV irradiation of several monocyclic β- and γ-(4-pentenyl)allyl alcohols in the presence of copper(I) trifluoromethanesulfonate (CuOTf) generates tricyclic cyclobutylcarbinyl alcohols. Efficient syntheses are reported for both 1- and 2-(hydroxymethyl)tricyclo[4.2.1.$0^{3,9}$]nonanes, as well as 2-(hydroxymethyl)tricyclo[4.3.1.$0^{3,10}$]decane, and for 3-(hydroxymethyl)tricyclo[5.3.0.$0^{1,4}$]decane (7). Solvolytic ring expansion of 7 and subsequent catalytic hydrogenation produces tricyclo[6.3.0.$0^{1,5}$]undecane, a ring system found in the sesquiterpenes isocomene and pentalenic acid.

Construction of a complex multicyclic carbon network is often a key challenge in the total synthesis of a natural product. To be of synthetic value, new methods of carbon skeletal construction must tolerate reactive functionality required in the final product or needed to facilitate transformations of synthetic intermediates. In the previous paper of this series[1] we reported that copper(I) trifluoromethanesulfonate (CuOTf) catalyzes clean and efficient [$2_\pi + 2_\pi$] photobicyclization of β- and γ-(4-pentenyl)allyl alcohols to produce bicyclo[3.2.0]heptyl derivatives, e.g., 1 and 2. The present study explores the applicability of



1



2

these new reactions for elaboration of complex tricyclic ring systems. Besides obvious potential applications for the total synthesis of natural products which incorporate a bicyclo[3.2.0]heptyl array,[2] such photobicyclizations may be of value for construction of other important multicyclic ring systems. Thus, the photoproducts are cyclobutylcarbinyl alcohols which may be useful intermediates for generating, via ring expansion,[3] tricyclic ring systems such as 5 from 3 via 4 or 8 from 6 via 7. Derivatives of 5 are important intermediates for total synthesis of gibberellic acids (n = 5)[4] and the alkaloids veatchine and garryine (n = 6),[5] and the sesquiterpenes isocomene[6] and pentalenic

(1) Salomon, R. G.; Coughlin, D. J.; Ghosh, S.; Zagorski, M. G. *J. Am. Chem. Soc.*, in press.

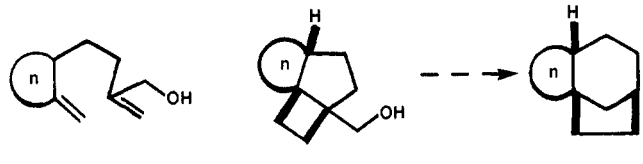
(2) Panasinsenes: (a) Yochihara, K.; Hirose, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2078. Cannabicyclol: (b) Gaoni, Y.; Mechoulam, R. *J. Am. Chem. Soc.* **1971**, *93*, 217–24. (c) Zalkow, L. H.; Harris, R. N., III; Van Deneer, D. *J. Chem. Soc., Chem. Commun.* **1977**, 456–7.

(3) Gutsche, C. D.; Redmore, D. "Carbocyclic Ring Expansion Reactions"; Academic Press: New York, 1968; pp 16–28.

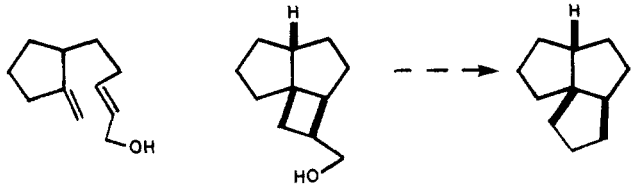
(4) (a) Harlow, R. L.; Simonsen, S. H. *Cryst. Struct. Commun.* **1977**, *6*, 689. (b) Taber, D. A. *Diss. Abstr. B* **1975**, *35*, 4399. (c) Corey, E. J.; Gorzynski Smith, J. *J. Am. Chem. Soc.* **1979**, *101*, 1038. (d) Stork, G.; Boeckman, R. K., Jr.; Taber, D. F.; Still, W. C.; Singh, J. *Ibid.* **1979**, *101*, 7107.

(5) (a) Masamune, S. *J. Am. Chem. Soc.* **1964**, *86*, 288. (b) *Ibid.* **1964**, *86*, 290.

0022-3263/82/1947-0829$01.25/0



3a, n = 5 4a, n = 5 5a, n = 5
3b, n = 6 4b, n = 6 5b, n = 6



6 7 8

acid[7] are derivatives of tricyclo[6.3.0.0^{1,5}]undecane (8).

Results and Discussion

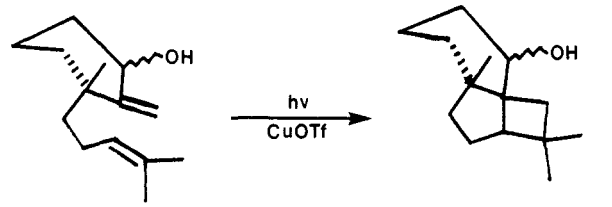
(A) Synthesis of Photobicyclization Substrates. Derivatives of 2-(Hydroxymethyl)-1,6-heptadiene. The monocyclic 2-(hydroxymethyl)-1,6-heptadiene derivative **3b** was prepared as outlined in Scheme I. Thus, 1-(hydroxymethyl)cyclohexene, readily prepared as outlined from ethyl 2-oxocyclohexanecarboxylate, is converted to the γ,δ-unsaturated ester **9** by the ortho ester Claisen rearrangement.[8] Reduction of **9** with $LiAlH_4$ provides alcohol **10** (R = H). The derived tosylate **10** (R = Ts) affords diester **11** by reaction with the sodium enolate of diethyl malonate. Reduction of the sodium enolate from **11** with $LiAlH_4$ in boiling glyme affords a 9:1 mixture of **3b** and **12**.

Another monocyclic substrate, **14**, incorporating the 2-(hydroxymethyl)-1,6-heptadiene array is prepared similarly (Scheme II). Thus, 3-(2-bromoethyl)cyclopentene, readily prepared as outlined from 2-cyclopentene-1-acetic acid, affords diester **13** by reaction with the sodium enolate of diethyl malonate. Reduction of the sodium enolate from **13** with $LiAlH_4$ in boiling glyme affords a 9:1 mixture of **14** and **15**.

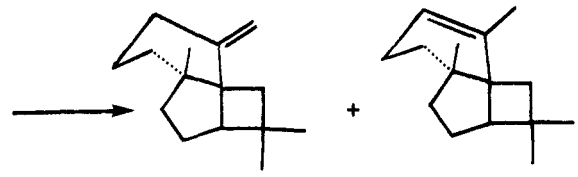
Derivatives of (*E*)-Octa-2,7-diene. Monocyclic substrates **6**, **23a**, and **23b** incorporating the (*E*)-octa-2,7-dien-1-ol array were prepared as outlined in Schemes III and IV. Thus, 1-(hydroxymethyl)cyclopentene (**16**), readily available as outlined in Scheme III, is converted to the ester **17** by the ortho ester Claisen rearrangement.[8] Reduction of **17** with $LiAlH_4$ provides alcohol **18**. Alkylation of 3-(α-ethoxyethoxy)-1-lithiopropyne with the derived tosylate **19** and hydrolysis of the product with aqueous acid gives the alcohol **20**. The propargyl alcohol **20** is reduced stereoselectively with lithium aluminum hydride to provide hydroxy diene **6**.

3-(β-Hydroxyethyl)cyclohexene (**21a**) is readily available from cyclohexene by metalation with *sec*-butyllithium and potassium *tert*-butoxide followed by alkylation with ethylene oxide.[9] The homologous 3-(β-hydroxyethyl)-cyclopentene (**21b**) is readily available from 2-cyclopentene-1-acetic acid by reduction with $LiAlH_4$. Treatment of these alcohols with PBr_3 affords the corresponding bromides **22**. These are transformed stereoselectively into hydroxy dienes **23** as outlined in Scheme IV, in analogy with Scheme III.

(B) Photobicyclizations. The great potential for copper-catalyzed photobicyclization in organic synthesis is already suggested by recent applications in other laboratories.[10,11] Our new synthetic method was recently applied as the key step in a total synthesis of α-panasinsine (**26**) and β-panasinsene (**27**), sesquiterpenes obtained from

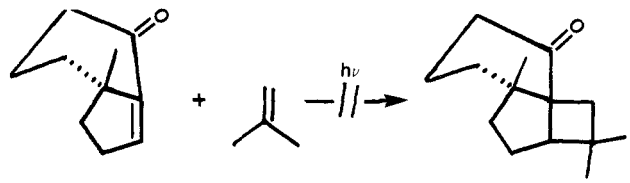


24 25



26 27

ginsing. Thus, the substrate **24**, which also incorporates the 2-(hydroxymethyl)-1,6-heptadiene array into a monocyclic skeleton affords **25** upon irradiation in the presence of CuOTf.[11] Significantly, an alternative synthetic approach to the requisite tricyclic ring system, based on photocycloaddition of isobutylene to an enone,[12] gave none of the required cycloadduct **28** under a variety of condi-



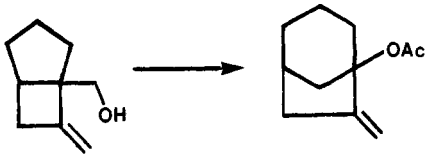
28

tions.[11] The hydroxyl functionality in **25** provides the necessary activation for completion of the panasinsene carbon skeleton by addition of a one carbon nucleophile.

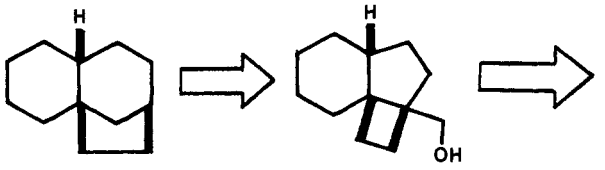
Solvolytic ring expansion of 1-(hydroxymethyl)bicyclo-[3.2.0]heptyl derivatives is known to provide bicyclo-[3.2.1]octyl derivatives in good yield, e.g., **29** → **30**.[13] Extension of this approach to the synthesis of a more complex ring system such as **5b** by ring expansion of **4b** requires photobicyclization of **3b**. Although **3b** was consumed upon irradiation in the presence of CuOTf, **4b** was not obtained. A complex mixture of *olefinic* products was formed. These were not characterized further.

In contrast, copper(I)-catalyzed photobicyclization is applicable to construction of the multicyclic carbon network of **31**. The substrate **14** also incorporates a 2-(hy-

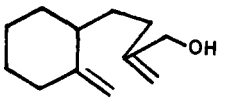
(6) Kaneda, M.; Takahashi, R.; Itaka, Y.; Shibato, S. *Tetrahedron Lett.* **1972**, 4609–11.
(7) Seto, H.; Sasaki, T.; Uzawa, J.; Takeuchi, S. *Tatrahedron Lett.* **1978**, 4411–4.
(8) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741–3.
(9) Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 453–65.
(10) Shih, C.; Fritzen, E. L.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 4462–71.
(11) McMurry, J. E.; Choy, W. *Tetrahedron Lett.* **1980**, 2477–80.
(12) For reviews, see the following: (a) Eaton, P. E. *Acc. Chem. Res.* **1968**, *1*, 50. (b) Bauslaugh, P. G. *Synthesis* **1970**, 287. (c) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41.
(13) Ziegler, F. E.; Kloek, J. A. *Tetrahedron Lett.* **1971**, 2261–4.



29 30

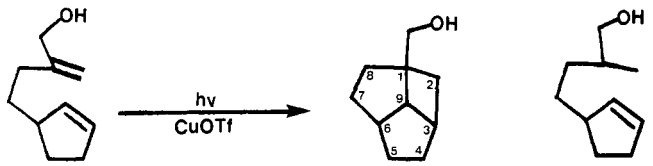


5b 4b



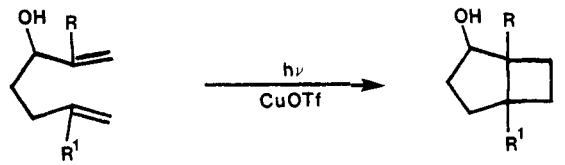
3b

droxymethyl)-1,6-heptadiene array into a monocyclic skeleton. A sample of diene 14 containing 10% of 15 was converted cleanly and quantitatively into a crude product consisting of 31 with unreacted 14. The structure 31



14 31 15

assumed for the photoproduct in analogy with the generation of 1 from 2-(hydroxymethyl)-1,6-heptadiene is consistent with its ^1H and ^{13}C NMR spectra (see Experimental Section). The contrasting behavior of **3b** and **14** can be understood in terms of greater steric hinderance of the **3b** → **4b** cyclization than for the **14** → **31** cyclization. The **3b** → **4b** cyclization requires generation of two new contiguous quaternary centers. A similar effect was found in the **32a** → **33a** photobicyclization which is sluggish



32a, R=R¹=Me **33a**, R=R¹=Me

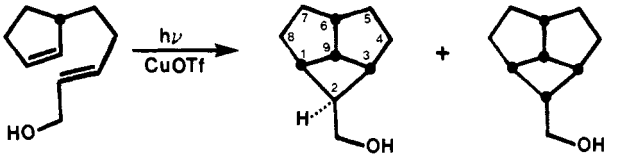
32b, R=Me, R¹=H **33b**, R=Me, R¹=H

32c, R=H, R¹=Me **33c**, R=H, R¹=Me

compared to the **32b** → **33b** or **32c** → **33c** photobicyclizations.[1] If photobicyclization is impeded for **3b**, competing alternative copper-catalyzed photoreactions of the allylic alcohol moiety are expected.[14]

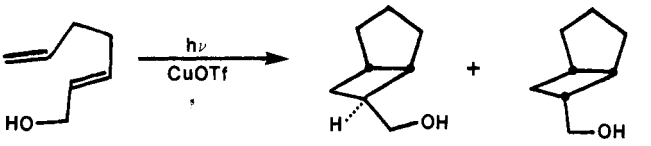
Irradiation of **23b** in the presence of CuOTf as catalyst affords 2-(hydroxymethyl)tricyclo[4.2.1.0^{3,9}]nonanes (**34**) in 93% yield after purification by distillation. Two epimeric products are formed in a 65:35 ratio. The ^{13}C NMR spectra of these photocycloadducts confirm their sym-

(14) Evers, J. T. M.; Mackor, A. *Tetrahedron Lett.* 1978, 821–4.



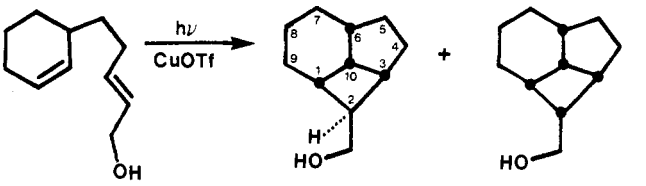
23b 34x 34n

metrical structures. Thus, only seven of the ten carbons in either epimer is magnetically nonequivalent. We assign the exo stereochemistry **34x** to the major epimer in analogy with the major product from **35** which was shown to have the exo configuration **2x**.[1] Furthermore, the chemical shift (δ 67.6) of the hydroxymethyl carbon in the major epimer **34x** is the same as that found for the corresponding carbon in **2x**. The hydroxymethyl carbon in the minor epimer **34n** absorbs at higher field (δ 59.9) similar to the endo epimer **2n** (δ 63.2).



35 2x 2n

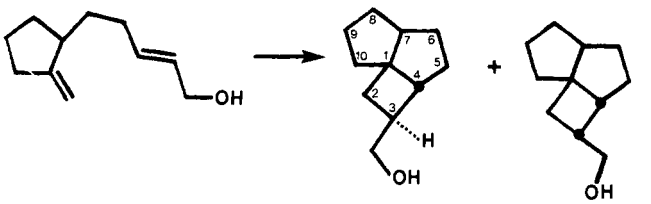
Copper-catalyzed intramolecular photocycloaddition of **23a** also gave two products in an 83:17 ratio which are assumed to be 2-(hydroxymethyl)tricyclo[4.3.1.0^{3,10}]decanes (**36**) in analogy with the **23a** → **34** photocyclization. The



23a 36x 36n

major isomer is assigned structure **36x** with an *exo*-hydroxymethyl substituent because of the chemical shift of the hydroxymethyl carbon (δ 67.3). The corresponding carbon in the minor isomer absorbs at higher field (δ 61.4) as expected (vide supra) for an *endo*-hydroxymethyl structure **36n**.

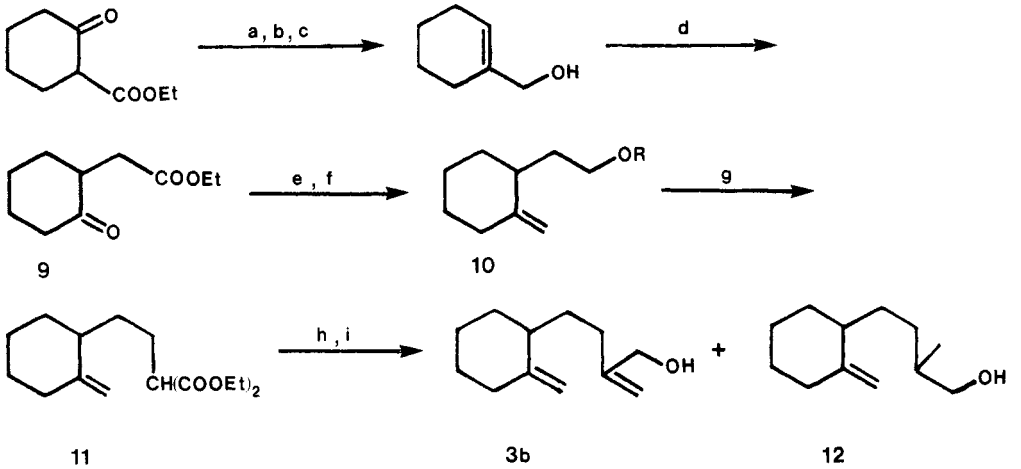
Hydroxy diene **6** also affords two intramolecular photocycloadducts in a 3:1 ratio upon irradiation in the presence of cuprous triflate. These are assigned epimeric structures **7x** and **7n** for the major and minor products,



6 7x 7n

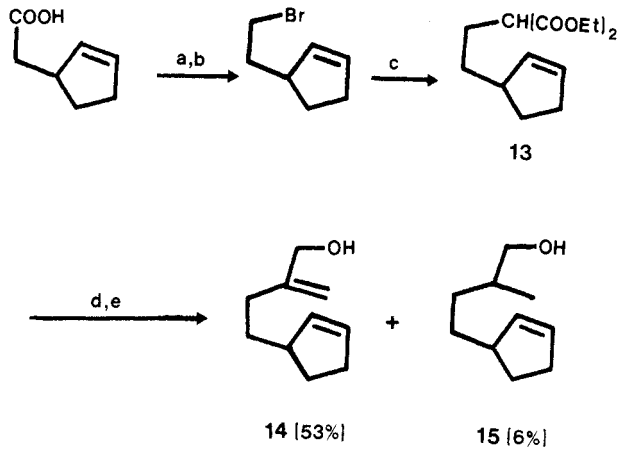
respectively, in analogy with the **35** → **2** cyclization. Again, the *exo*-hydroxymethyl structure **7x** is presumed on the basis of the chemical shift (δ 67.9) of the hydroxymethyl carbon in the major isomer. The *endo*-hydroxymethyl structure **7n** is presumed for the minor isomer for which the corresponding carbon absorbs at higher field (δ 63.9). It seems reasonable that the chemical shift of the hydroxymethyl carbon in the exo isomers **2x**, **34x**, **36x**, and **7x** would all be virtually the same (δ 67.6 ± 0.3) whereas

Scheme I[a]



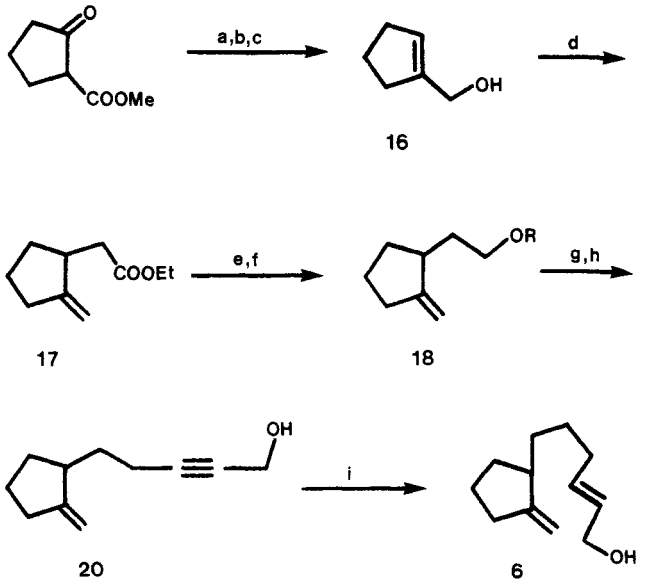
[a] (a) $NaBH_4$, (b) TsCl/Py/115 °C, (c) $Li(EtO)_2AlH_2$, (d) $MeCH(OEt)_3$/EtCOOH, (e) $LiAlH_4$, (f) TsCl/Py/0 °C, (g) $NaCH(COOEt)_2$, (h) NaH, (i) $LiAlH_4$/glyme.

Scheme II[a]



[a] (a) $LiAlH_4/Et_2O$, (b) PBr_3, (c) $NaCH(COOEt)_2$, (d) NaH, (e) $LiAlH_4$/glyme.

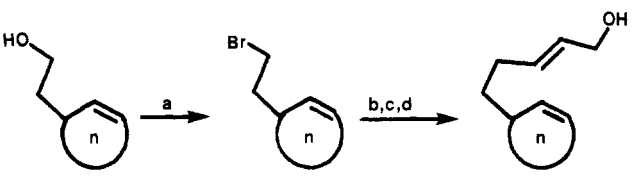
Scheme III[a]



[a] (a) $NaBH_4$, (b) TsCl/Py/115 °C, (c) $Li(EtO)_2AlH_2$, (d) $MeCH(OEt)_3$/EtCOOH, (e) $LiAlH_4$, (f) TsCl/Py/0 °C, (g) $LiC{\equiv}CCH_2OR$, (h) H^+/H_2O/THF, (i) $LiAlH_4$/THF.

the chemical shifts of the hydroxymethyl carbon in the corresponding endo epimers range from δ 59.9 to 63.9.

Scheme IV[a]



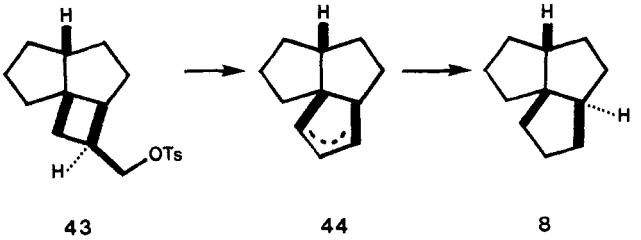
21a, n=6 22a, n=6 23a, n=6
21b, n=5 22b, n=5 23b, n=5

[a] (a) PBr_3, (b) $LiC{\equiv}CCH_2OR$, (c) H^+/H_2O/THF, (d) $LiAlH_4$/THF.

Thus, the endo groups are subject to greater variations in local structural environment than are the *exo*-hydroxymethyl groups.

Four different strategies have been employed for elaboration of the tricyclo[6.3.0.$0^{1,4}$]undecane ring system during total syntheses of isocomene **37**[15] (Scheme V). These include ring contraction of a cyclohexanone ring precursor (**38**) derived, in turn, by intramolecular ene cyclization from a bicyclic precursor (**39**).[16] Cyclialkylation of unsaturated bicyclic aldehyde **40** generates the requisite ring system directly[17] as does acid-catalyzed cyclization of epoxy olefin **41**.[18] However, structural characterization of the products derived from **41** have been questioned.[17] Acid-catalyzed rearrangement of the vinylcyclobutane **42** produces isocomene (**37**) in excellent yield.[19]

As a model of an alternative approach for construction of the tricyclo[6.3.0.$0^{1,5}$]undecane (**8**) ring system of isocomene, solvolytic ring expansion of **7** was examined. A tosylate **43** prepared from **7x** afforded an alkene, **44**, upon

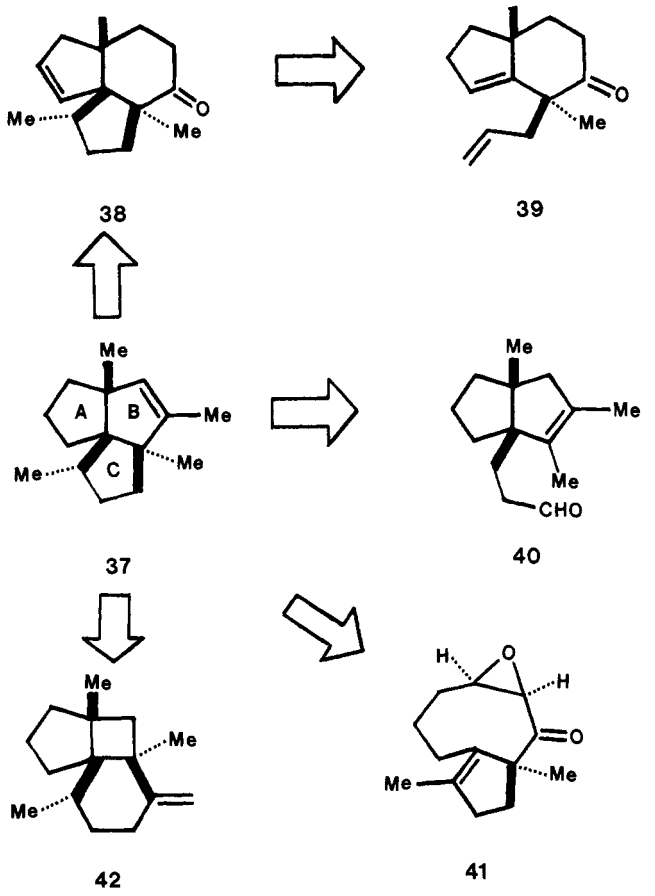


43 44 8

(15) We suggest the designation of rings A–C as indicated for **37** in Scheme V.

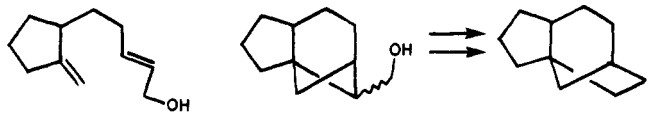
(16) Oppolzer, W.; Battig, K.; Hudlicky, T. *Helv. Chim. Acta* **1979**, *62*, 1493–6.
(17) Paquette, L. A.; Han, Y. K. *J. Org. Chem.* **1979**, *44*, 4014–6.
(18) Chatterjee, S. *J. Chem. Soc., Chem. Commun.* **1979**, 620–1.
(19) Pirrung, M. C. *J. Am. Chem. Soc.* **1981**, *103*, 82–7.

Scheme V



heating in acetic acid. Catalytic hydrogenation of **44** gave the hydrocarbon **8**. The ^{13}C NMR spectrum of this hydrocarbon confirms its symmetrical structure. Thus, only six of the eleven carbons in **8** are magnetically nonequivalent owing to a C_2 axis of symmetry.

This synthesis of **8** from **6** via photobicyclization–ring expansion also rules out the alternative mode **6** → **45** for the photobicyclization. Thus, ring expansion of **45** followed by catalytic hydrogenation would have provided an unsymmetrical hydrocarbon **46** instead of the symmetrical hydrocarbon **8**.



Summary

Photobicyclization catalyzed by CuOTf provides a novel and often efficient synthetic method for construction of complex multicyclic carbon networks. The reaction tolerates reactive allylic hydroxyl functionality and can be used to generate tricyclic cyclobutylcarbinyl alcohols. These products are susceptible to solvolytic ring expansion. The combination of photobicyclization and solvolytic ring expansion was exploited to construct the tricyclo[6.3.0.0^{1,5}]undecane ring system found in the sesquiterpenes isocomene and pentalenic acid. However, elaboration of tricyclic synthons for gibberellic acids or the alkaloids veatchine and garryine was prevented by the failure of the requisite photobicyclization presumably owing to steric hinderance which impedes generation of two new contiguous quaternary centers.

Experimental Section[20]

Ethyl (2-Methylenecyclohexyl)acetate (9). A mixture containing (1-cyclohexenyl)methanol (11.2 g, 0.1 mol), triethyl orthoacetate (113 g, 128 mL, 0.7 mol), and propionic acid (0.44 g, 6 mmol) was heated at 138 °C (external) for 18 h with slow distillative removal of the ethanol produced. After the mixture was cooled to room temperature, propionic acid and excess triethyl orthoacetate were removed by distillation under reduced pressure [50–60 °C (15 mm)]. The title compound (14.0 g, 77% yield) was then distilled: bp 116–119 °C (13 mm); ^1H NMR ($CDCl_3$) δ 1.26 (3 H, t, J = 7 Hz), 1.2–2.8 (11 H), 4.17 (2 H, q, J = 7 Hz), 4.58 (1 H), 4.70 (1 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; 4, 9.95. Found: C, 72.54; H, 10.06.

2-(2-Methylenecyclohexyl)ethanol (10, R = H). In a 1-L, three-necked, round-bottomed flask fitted with a mechanical stirrer, Friedrichs condenser, and pressure-equalizing addition funnel were placed $LiAlH_4$ (7.3 g, 0.144 mol) and dry ether (250 mL). The ester **9** (24 g, 0.13 mol) in ether (70 mL) was added dropwise at such a rate as to maintain a gentle reflux. After completion of the addition, the mixture was boiled under reflux with stirring for 3 h. After the mixture cooled, the reaction was quenched by careful dropwise addition of water (7 mL), 15% NaOH (7 mL), and water (14 mL). The resulting white suspension was filtered on a sintered-glass Buchner funnel with suction, and the filter cake was thoroughly triturated with ether (3 × 50 mL). The organic solution was dried (Na_2SO_4), concentrated by rotary evaporation, and distilled under reduced pressure to provide alcohol **10**: 14.1 g (77% yield); bp 108–110 °C (13 mm): ^1H NMR ($CDCl_3$) δ 1.1–2.5 (2 H), 3.70 (2 H, t, J = 7 Hz), 4.68 (2 H).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.98; H, 11.51.

2-[2-(β-Toluenesulfonyloxy)ethyl]-1-methylenecyclohexane (10, R = Ts). A solution containing *p*-toluenesulfonyl chloride (7.6 g, 40 mmol) in benzene (20 mL) and 2-(2-methylenecyclohexyl)ethanol (5.6 g, 6.2 mL, 40 mmol) was treated with pyridine (4.2 g, 4.3 mL, 48 mmol) at 0 °C, and the mixture was then kept in the refrigerator at 5 °C for 15 h and finally allowed to stand at 20 °C for 3 days. Precipitated pyridinium hydrochloride was removed by vacuum filtration and washed with benzene. The combined filtrates were washed with cold 10% HCl (40 mL), water (40 mL), and saturated aqueous NaCl (40 mL) and dried (Na_2SO_4). The crude product obtained after removal of solvent by rotary evaporation was chromatographed on silica gel (440 g) with $CHCl_3$ as the eluting solvent. Removal of solvent by rotary evaporation and finally with a high-vacuum pump (0.02 mm) gave purified tosylate (8.2 g, 70%) which was used without further purification: ^1H NMR ($CDCl_3$) δ 1.1–2.3 (11 H), 2.46 (3 H, s), 4.10 (2 H, t, J = 6.5 Hz), 4.48 (1 H), 7.37 (2 H, d, J = 8.5 Hz), 7.83 (2 H, d, J = 8.5 Hz).

Diethyl [2-(2-Methylenecyclohexyl)ethyl]propanedioate (11). In a 50-mL, round-bottomed flask fitted with a mechanical stirrer and reflux condenser and topped with a head of dry nitrogen was placed anhydrous ethanol (13 mL). Sodium (0.69 g, 30 mmol) was added. After the resulting solution of sodium ethoxide was allowed to cool to 50 °C, diethyl malonate (4.7 mL, 31 mmol) was added in one portion followed by dropwise addition of the tosylate **10** (5.9 g, 20 mmol). The resulting mixture was boiled under reflux for 3 h, cooled, combined with cold aqueous 5% HCl (100 mL), and extracted with ether (3 × 75 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ (100 mL), saturated aqueous NaCl (50 mL), and dried (Na_2SO_4). Removal of solvent by rotary evaporation followed by distillation under reduced pressure afforded **11**: 4.6 g (82% yield); bp 111–115 °C (0.04 mm); ^1H NMR ($CDCl_3$) δ 1.27 (6 H, t, J = 7 Hz), 1.2–2.3 (13 H), 3.34 (1 H, t, J = 7 Hz), 4.22 (4 H, q, J = 7 Hz), 4.62 (1 H), 4.69 (1 H).

Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found: C, 68.06; H, 9.23.

2-Methylene-4-(2-methylenecyclohexyl)butanol (3b). A suspension of 57% NaH in mineral oil (0.98 g) was washed with pentane (2 × 20 mL) and then suspended with mechanical stirring in 1,2-dimethoxyethane (25 mL) freshly distilled from sodium

(20) For general procedures and materials preparation see ref 1.

benzophenone ketyl. Malonate **11** (4.5 g, 16 mmol) was added, and the mixture was stirred and maintained at reflux for 6 h. After cooling, $LiAlH_4$ (0.16 g) was added cautiously with stirring. After the initial exothermic reaction subsided, the mixture was boiled under reflux for 3 h. After the mixture cooled, ethyl formate (5.8 mL) was cautiously added dropwise, and the resulting mixture was stirred and boiled under reflux for 1 h. After this mixture cooled, water (1.5 mL), 15% NaOH (1.5 mL), and water (3 mL) were cautiously added dropwise in succession. The mixture was cooled to 20 °C, ether (40 mL) was added, and the resulting mixture was stirred for 1 h at 20 °C and then filtered with suction on a sintered-glass Buchner funnel. The filter cake was thoroughly triturated with ether (2 × 20 mL), and the combined organic solution was concentrated by rotary evaporation. Distillation of the residual oil under reduced pressure affords **3b** [1.8 g (63% yield); bp 85–92 °C (0.05 mm)] which contained about 10% of **12** as evidenced by a doublet (J = 6 Hz) at δ 0.91 in the ^1H NMR ($CDCl_3$) spectrum of **3b**: δ 0.9–2.3 (14 H), 4.10 (2 H, s), 4.60 (H), 4.68 (H), 4.92 (1 H), 5.05 (1 H).

Diethyl [2-(2-Cyclopenten-1-yl)ethyl]propanedioate (13). A solution of (2-cyclopenten-1-yl)acetic acid (20.0 g, 0.158 mol) in THF (400 mL) was added dropwise under dry nitrogen to a mechanically stirred suspension of lithium aluminum hydride (6 g, 0.158 mol) in THF (100 mL). After completion of the addition, the mixture was boiled under reflux for 2 h. Then water (6 mL), 15% NaOH (6 mL), and water (18 mL) were cautiously added in succession with stirring. The resulting white suspension was filtered with suction through a sintered-glass Buchner funnel. The filter cake was thoroughly triturated with ether (2 × 50 mL), and the combined organic solutions were concentrated by rotary evaporation of the solvents. Distillation of the residual oil afforded 2-(2-cyclopenten-1-yl)ethanol (**21b**): 13.2 g (75% yield); bp 59–62 °C (2 mm).

A solution of freshly distilled PBr_3 (3.0 mL, 32 mmol) in dry benzene (5 mL) was treated dropwise under dry nitrogen with dry pyridine (1.3 mL). After the resulting mixture was stirred for 15 minutes, the mixture was cooled to −5 °C, and then a mixture of 2-(2-cyclopenten-1-yl)ethanol (10 g, 89 mmol) and pyridine (0.5 mL) was added dropwise over 1 h at −5 to +5 °C. After being allowed to stand 40 h, the mixture was transferred into a 50-mL, round-bottomed flask with a little benzene for rinsing the reaction flask. The benzene solvent was then removed by distillation under reduced pressure [bp ~30 °C (60 mm)] and 3-(2-bromoethyl)cyclopent-1-ene (**22b**; 9.2 g, 60% yield) was collected at ~70 °C (13 mm) with an oil bath temperature of 90–120 °C.

Alkylation of diethyl malonate with the above bromide **22b** was achieved in analogy to the preparation of diethyl (4-pentenyl)-propanedioate from 5-bromo-1-pentene.[1] The title compound **13** was obtained in 85% yield: bp 110–114 °C (0.03 mm); ^1H NMR ($CDCl_3$) δ 1.26 (6 H, t, J = 7 Hz), 1.3–2.5 (9 H), 3.30 (1 H, t, J = 7 Hz), 4.18 (4 H, q, J = 7 Hz), 5.73 (2 H).

Anal. Calcd for $C_{14}H_{22}O$: C, 66.11; H, 8.72. Found: C, 66.02; H, 8.79.

3-[3-(Hydroxymethyl)-3-butenyl]cyclopentene (14). The diester **13** was converted into 90% pure **14** by treatment with NaH and then $LiAlH_4$ in a procedure analogous to that employed in the synthesis of **3b** above. The reduction product was obtained in 59% yield [bp 78–83 °C (0.05 mm)] and contained the title compound as well as ~10% of 4-(1-cyclopenten-3-yl)-2-methylbutan-1-ol (**15**) as evidenced by a doublet (J = 6 Hz) at δ 0.91 in the ^1H NMR ($CDCl_3$) spectrum of **14**: δ 1.2–2.9 (10 H), 4.08 (2 H, s), 4.89 (1 H, s), 5.03 (1 H, s), 5.72 (2 H).

(Cyclopenten-1-yl)methanol (16). Reduction of 2-carbethoxycyclopentanone to produce 2-carbethoxycyclopentanol[21] and conversion of the latter into 1-carbethoxycyclopentene[22] was performed as described previously. In a 2-L, three-necked flask fitted with a Friedricks condenser, mechanical stirrer, and pressure-equalizing addition funnel topped with a head of dry nitrogen were placed $LiAlH_4$ (12.2 g, 0.24 mol) and dry ether (400 mL). Absolute ethanol (14.8 g, 18.7 mL, 0.24 mol) was added cautiously dropwise. After completion of the addition, the mixture was boiled under reflux for 1 h. Then 1-carbethoxycyclopentene (26.6 g, 0.214 mol) was added dropwise at such a rate as to maintain a gentle reflux. After completion of the addition, THF (100 mL) was added, and the resulting mixture was again boiled under reflux for 3 h, cooled, and then quenched by careful dropwise addition of water (12 mL), 15% NaOH (12 mL), and water (30 mL) in succession. The resulting white suspension was filtered with suction on a sintered-glass Buchner funnel. The filter cake was throughly triturated with ether (2 × 50 mL), and the combined organic extracts were concentrated by rotary evaporation of the solvents. Distillation of the residual oil under reduced pressure afforded **16**: 19.6 g (93% yield); bp 59–17 °C (15 mm) [lit.[23] bp 75 °C (20 mm)].

Ethyl [(2-Methylenecyclopentyl)methyl]acetate (17). (Cyclopenten-1-yl)methanol (19.6 g, 0.2 mol), triethyl orthoacetate (200 mL, 1.1 mol), and propionic acid (1 mL) were heated at 138 °C for 10 h with distillative removal of the ethanol formed. After the mixture was cooled to room temperature, propionic acid and excess ortho ester were removed by distillation under aspirator vacuum (~50–60 °C). Then the residue was distilled to afford **17** (21.6 g). The pot residue was recombined with the excess ortho ester and propionic acid and heated again at 138 °C as above, affording after 15 h an additional 5.6 g of product for a total of 27.2 g (81% yield) of **17**: bp 96–98 °C (15 mm); ^1H NMR ($CDCl_3$) δ 1.25 (3 H, t, J = 7 Hz), 1.4–3.0 (9 H), 4.15 (2 H, q, J = 7 Hz), 4.85 (2 H, m).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.21; H, 9.55.

1-(β-Hydroxyethyl)-2-methylenecyclopentane (18, R = H). In a 1-L, three-necked, round-bottomed flask fitted with a mechanical stirrer, Friedricks condenser, and pressure-equalizing addition funnel were placed $LiAlH_4$ (9.18, 0.18 mol) and dry ether (300 mL). The ester **17** (26.9 g, 0.16 mol) in ether (100 mL) was added dropwise at such a rate as to maintain a gentle reflux. After completion of the addition, the mixture was boiled under reflux with stirring for 3 h. After the mixture cooled, the reaction was cautiously quenched with water (9 mL), 15% NaOH (9 mL), and water (23 mL) and filtered, and the filter cake was thoroughly triturated with ether (2 × 50 mL). The organic solution was dried (Na_2SO_4) and concentrated by rotary evaporation of the solvents, and the residue was distilled under reduced pressure to afford **18** (R = H): 19.6 g (97%); bp 98–101 °C (15 mm); ^1H NMR ($CDCl_3$) δ 1.1–2.1 (7 H), 2.15–2.65 (3 H), 3.73 (2 H, t, J = 7 Hz), 4.87 (2 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.19; H, 11.05.

2-[β-(p-Toluenesulfonyloxy)ethyl]-1-methylenecyclopentane (18, R = Ts). A solution containing p-toluenesulfonyl chloride (19.1 g, 0.10 mol) and 2-(β-hydroxyethyl)-1-methylenecyclopentane (12.6 g, 13.55 mL, 0.10 mol) in dry benzene (50 mL) was treated with dry pyridine (10.6 g, 10.8 mL, 0.12 mol) at 0 °C with magnetic stirring, and the resulting mixture was kept at 5 °C (refrigerater) overnight and at 20 °C for 3 days. Precipitated pyridinium hydrochloride was removed by vacuum filtration with a sintered-glass Buchner funnel and washed with benzene. The combined filtrate and washings were washed with cold aqueous 10% HCl (100 mL), water (100 mL), and saturated aqueous NaCl (100 mL) and dried (Na_2SO_4). Removal of solvent by rotary evaporation and finally with a high-vacuum pump (0.02 mm) gave crude tosylate (23.8 g, 85%) which was used without further purification: ^1H NMR ($CDCl_3$) δ 1.0–2.5 (9 H), 2.46 (3 H, s), 4.13 (2 H, t, J = 6.5 Hz), 4.70 (1 H, m), 4.87 (1 H, m), 7.37 (2 H, d, J = 8 Hz), 7.84 (2 H, d, J = 8 Hz).

2-[5-(α-Ethoxyethoxy)-3-pentyn-1-yl]-1-methylenecyclopentane. In a 250-mL, round-bottomed, three-necked flask with a magnetic stirrer, thermometer, rubber septum, and reflux condenser topped with a head of dry nitrogen were placed THF (60 mL) and triphenylmethane (30 mg). A few drops of n-BuLi in hexane were added until a red color developed. Then α-ethoxyethyl propargyl ether (9.3 mL, 63 mmol) followed by n-BuLi (39 mL of a 1.6 N solution, 63 mmol) was added at 0 °C until a red color developed again. This was discharged with an additional drop of propargyl ether. Hexamethylphosphoramide (9 mL)

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(22) Kroenthal, R. L.; Becker, E. I. *J. Am. Chem. Soc.* **1957**, *79*, 1095.
(23) Pal, P. R.; Skinner, C. G.; Dennis, R. L.; Shive, W. L. *J. Am. Chem. Soc.* **1956**, *78*, 5116–8.

followed by 18 (R = OTs; 12.2 g, 11.0 mL, 44 mmol) was then added, the rubber septum was replaced by a glass stopper, and the resulting mixture was boiled under reflux overnight. After cooling, the mixture was poured into ice–water (100 mL) and extracted into pentane (3 × 100 mL). The combined extracts were washed with water (3 × 50 mL) and dried (Na_2SO_4), and the solvents were removed by rotary evaporation. The residue was distilled under reduced pressure to afford the title compound: 7.7 g (75%); bp 99–102 °C (0.06 mm); ^{1}H NMR ($CDCl_3$) δ 1.19 (3 H, t, J = 7 Hz), 1.32 (3 H, d, J = 5 Hz), 1.4–2.6 (11 H), 3.60 (2 H, m), 4.20 (2 H, t, J = 2 Hz), 4.7–5.0 (3 H).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.36; H, 10.31.

2-(5-Hydroxy-3-pentyn-1-yl)-1-methylenecyclopentane (20). A solution of 2-[5-(α-ethoxyethoxy)pent-3-yn-1-yl]-1-methylenecyclopentane (7.44 g, 32 mmol) and pyridinium p-toluenesulfonate[24] (0.83 g, 3.2 mmol) in methanol (165 mL) and water (16.5 mL) was boiled under reflux for 2 h. After the mixture cooled, methanol was removed by rotary evaporation, and the residue was extracted with ether (300 mL). The extract was washed with half-saturated NaCl (100 mL) and dried (Na_2SO_4), and the solvents were removed by rotary evaporation. Distillation of the residue afforded **20**: 5.2 g (100%); bp 97–99 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 0.9–2.6 (12 H), 4.25 (2 H, t, J = 2 Hz), 4.85 (2 H, m).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.61; H, 9.73.

2-(5-Hydroxy-(Z)-3-penten-1-yl)-1-methylenecyclopentane (6). A suspension of $LiAlH_4$ (5 g) in THF (220 mL) in a three-necked round-bottomed flask fitted with a mechanical stirrer and reflux condenser topped with a head of dry nitrogen was treated with alkynol **20** (4.9 g, 30 mmol) dropwise with mechanical stirring. The resulting mixture was boiled under reflux for 4 h. Then, with ice–water cooling, were added water (5 mL), 15% NaOH (5 mL), and water (10 mL) cautiously in succession. The resulting white suspension was filtered with suction through a sintered-glass Buchner funnel. The filter cake was thoroughly triturated with ether (2 × 50 mL), and the combined organic solutions were concentrated by rotary evaporation of the solvents. Distillation of the residue under reduced pressure afforded **6**: 4.3 g (86%); bp 84–86 °C (0.03 mm); ^{1}H NMR ($CDCl_3$) δ 0.9–2.6 (12 H), 4.10 (2 H, m), 4.84 (2 H, m), 5.72 (2 H, m).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.41. Found: C, 79.27; H, 10.83.

5-(2-Cyclohexen-1-yl)-1-(α-ethoxyethoxy)-2-pentyne. Bromide **22a** was prepared from 2-(2-cyclohexen-1-yl)ethanol[9] (**21a**) by a procedure analogous to that used for the **21b** → **22b** conversion (vide supra). The crude bromide [bp 50–70 °C (0.2 mm)] was obtained in 52% yield. In a 100-mL, three-necked, round-bottomed flask with a magnetic stirrer, thermometer, rubber septum, and reflux condenser topped with a head of dry nitrogen were placed THF (40 mL) and triphenylmethane (20 mg). A few drops of n-BuLi in hexane were added until a red color developed. Then α-ethoxyethyl propargyl ether (6.2 mL, 42 mmol) followed by n-BuLi (26.4 mL of a 1.6 N solution, 42 mmol) was added at 0 °C until a red color developed again. This was discharged with an additional drop of propargyl ether. Then hexamethylphosphoramide (6 mL) followed by bromide **22a** (7.6 g, 40 mmol) was added, the rubber suptum was replaced by a glass stopper, and the resulting mixture was boiled under reflux overnight. After cooling, the mixture was poured into ice–water (100 mL) and extracted into pentane (3 × 100 mL). The combined extracts were washed with water (3 × 50 mL) and dried (Na_2SO_4), and the solvents were removed by rotary evaporation. The residue was distilled under reduced pressure to afford the title compound: 8.3 g (88%); bp 115–116 °C (0.07 mm); ^{1}H NMR ($CDCl_3$) δ 1.20 (3 H, t, J = 7 Hz), 1.28 (3 H, d, J = 5.3 Hz), 1.2–2.4 (11 H), 3.60 (2 H, m), 4.21 (2 H, t, J = 2.2 Hz), 4.86 (1 H, q, J = 5.3 Hz), 5.65 (2 H, apparent t).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.24, H, 10.12.

5-(2-Cyclohexen-1-yl)-2-pentyn-1-ol. A solution of 5-(2-cyclohexen-1-yl)-1-(α-ethoxyethoxy)-2-pentyne (7.8 g, 33 mmol) in methanol (40 mL), water (11 mL), and concentrated HCl (4 mL) was boiled under reflux for 3 h. After the mixture cooled, methanol was removed by rotary evaporation. The crude product was extracted into ether (2 × 100 mL). The extracts were washed with water (20 mL) and saturated aqueous NaCl (20 mL), dried (Na_2SO_4), and concentrated by rotary evaporation of the solvents. Distillation of the residue under reduced pressure gave the title propargyl alcohol: 5.4 g (97%); bp 93.94 °C (0.03 mm); ^{1}H NMR ($CDCl_3$) δ 0.9–2.5 (12 H), 4.25 (2 H, br s), 5.52 J = H, d, J = 10 Hz), 5.84 (1 H, d, J = 10 Hz).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: 80.47; H, 9.75.

5-(2-Cyclohexen-1-yl)-(E)-2-penten-1-ol (23a). Reduction of 5-(2-cyclohexen-1-yl)-2-pentyn-1-ol (2.52 g, 2.56 mL, 15 mmol) with $LiAlH_4$ (2.5 g) in THF (110 mL) was performed by a procedure analogous with that used for conversion of **20** to **6**. The E olefin **23a** (2.1 g, 82%) obtained shows the following: bp 94–95 °C (0.04 mm); ^{1}H NMR ($CDCl_3$) δ 1.1–2.4 (21 H), 4.11 (2 H, d, J = 3 Hz), 5.7 (4 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.33; H, 11.02.

5-(2-Cyclopenten-1-yl)-1-(α-ethoxyethoxy)-2-pentyne. The title compound was prepared from bromide **22b** (vide supra) in 96% yield by a procedure analogous to that described above for the cyclohexenyl homologue. The title compound shows the following: bp 148–152 °C (15 mm); ^{1}H NMR ($CDCl_3$) δ 1.20 (3 H, t, J = 7 Hz), 1.34 (3 H, d, J = 5.5 Hz), 1.3–2.5 (8 H), 2.77 (1 H, br t, J = 7 Hz), 3.60 (2 H, m), 4.20 (2 H, t, J = 2 Hz), 4.86 (1 H, q, J = 5.5 Hz), 5.73 (2 H).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 99.7. Found: C, 75.58; H, 10.13.

5-(2-Cyclopenten-1-yl)-2-pentyn-1-ol. The title compound was prepared from the above α-ethoxyethyl ether in 94% yield by a procedure analogous to that described above for the cyclohexenyl homologue. The title propargyl alcohol shows the following: bp 120–122 °C (15 mm); ^{1}H NMR ($CDCl_3$) δ 1.2–2.5 (9 H), 2.5–3.1 (1 H), 4.25 (2 H, t, J = 2.5 Hz), 5.72 (2 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.11; H, 9.37.

5-(2-Cyclopenten-1-yl)-(E)-2-penten-1-ol (23b). The title compound was prepared from the above propargyl alcohol in 96% yield by a procedure analogous to that described above for the cyclohexenyl homologue. The title allylic alcohol shows the following: bp 130 °C (15 mm); ^{1}H NMR ($CDCl_3$) δ 1.2–2.9 (10 H), 4.11 (2 H, m), 5.74 (4 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.78; H, 10.55.

2-(Hydroxymethyl)tricyclo[5.1.1.0^{4,8}]nonane (31). Photobicyclization[20] of 3-[3-(hydroxymethyl)-3-butenyl]cyclopentene (**14**; 5.7 g, 37 mmol) containing ~10% of 4-(1-cyclopenten-3-yl)-2-methylbutan-1-ol (**15**) in ether (200 mL) and methanol (2 mL) in the presence of $(CuOTf)_2{\cdot}C_6H_6$ (0.31 g) for 18 h provided **31** [5.5 g (96%); bp 89–92 °C (0.04 mm)] which contained ~10% of **15**. The tricyclic product **31** is readily isolable by gas–liquid phase chromatography on a 5 ft × 0.25 in. column packed with 10% Dow Corning 710 silicone oil on 60/80 Chromosorb W at 200 °C. The tricyclononane **31** shows the following: ^{1}H NMR ($CDCl_3$) δ 1.0–2.7 (14 H), 3.55 (2 H, s); ^{13}C NMR ($CDCl_3$) δ 69.3 (t, CH_2OH), 51.1 (d), 46.7 (s, C-2), 45.0 (d), 36.1 (t), 35.0 (t), 33.8 (t), 32.6 (t), 32.4 (t), 31.5 (d).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.82; H, 10.45.

2-(Hydroxymethyl)tricyclo[4.2.1.0^{3,9}]nonanes (34). Photobicyclization[20] (vide supra) of 5-(2-cyclopenten-1-yl)-(E)-2-penten-1-ol (**23b**; 4.0 g, 26 mmol) in ether (200 mL) in the presence of $(CuOTf)_2{\cdot}C_6H_6$ (0.22 g) provided **34** [3.7 g (93% yield); bp 81–86 °C (0.3 mm)] which is a 65:35 mixture of C-2 epimers. These are readily separable by gas–liquid phase chromatography at 220 °C on a 4 ft × 0.25 in. column packed with 15% FFAP on 60/80 Chromosorb W. Relative retention times of the major and minor epimers **34x** and **34n** are 1.00 and 1.41, respectively.

***exo*-2-(Hydroxymethyl)tricyclo[4.2.1.0^{3,9}]nonane (34x):** ^{1}H NMR ($CDCl_3$) δ 1.3–1.9 (9 H), 1.9–2.4 (2 H), 2.4–3.1 (3 H), 3.67 (2 H, d, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 67.6 (t, CH_2OH), 49.3 (d), 47.2 (d), 44.7 (d), 37.8 (d), 33.4 (t), 32.9 (t).

(24) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772–4.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.79; H, 10.62.

***endo*-2-(Hydroxymethyl)tricyclo[4.2.1.0^{3,9}]nonane (34n)**: ^{1}H NMR ($CDCl_3$) δ 1.3–2.0 (9 H), 2.0–3.0 (4 H), 3.5–4.9 (3 H); ^{13}C NMR ($CDCl_3$) δ 59.9 (t, CH_2OH), 48.3 (d), 44.8 (d), 37.1 (d), 36.7 (d), 33.9 (t), 26.9 (t).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.85; H, 10.53.

2-(Hydroxymethyl)tricyclo[4.3.1.0^{3,10}]decanes (36). Photobicyclization[20] (vide supra) of 5-(2-cyclohexen-1-yl)-(*E*)-2-penten-1-ol (**23a**) in the presence of $(CuOTf)_2{\cdot}C_6H_6$ provided **36** [94% yield; bp 95–101 °C (0.2 mm)] which was a 72:28 mixture of C-2 epimers. These are preparatively separable by gas–liquid phase chromatography at 240 °C on a 5 ft × 0.25 in. column packed with 10% Apiezon L on 60/80 Chromosorb W. Relative retention times of the major and minor epimers **36x** and **36n** are 1.0 and 1.2, respectively.

***exo*-2-(Hydroxymethyl)tricyclo[4.3.1.0^{3,10}]decane (36x)**: ^{1}H NMR ($CDCl_3$) δ 1.3–2.6 (16 H), 3.59 (2 H, d, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 67.3 (t, CH_2OH), 41.2 (d), 35.5 (d), 34.9 (d), 32.2 (t), 31.1 (d), 30.2 (t), 26.6 (t), 25.9 (t), 15.9 (t).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.53; H, 11.04.

***endo*-2-(Hydroxymethyl)tricyclo[4.3.1.0^{3,10}]decane (36n)**: ^{1}H NMR ($CDCl_3$) δ 1.1–2.4 (12 H), 2.4–3.1 (4 H), 3.75–3.95 (2 H); ^{13}C NMR ($CDCl_3$) δ 61.4 (t, CH_2OH), 40.8 (d), 40.6 (d), 38.2 (d), 35.8 (d), 35.9 (d), 30.1 (d), 29.2 (t), 25.8 (t), 27.7 (t), 19.9 (t).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.50; H, 10.85.

3-(Hydroxymethyl)tricyclo[5.3.0.0^{1,4}]decane (7). Photobicyclization[20] (vide supra) of 2-(5-hydroxy-(*Z*)-3-penten-1-yl)-1-methylenecyclopentane (**6**) in the presence of $(CuOTf)_2{\cdot}C_6H_6$ provided **7** (91% yield) which was a 3:1 mixture of C-3 epimers. These are preparatively separable by gas–liquid phase chromatography at 150 °C on a 4 ft × 0.25 in. column packed with 15% FFAP on 60/80 Chromosorb W. Relative retention times of the major and minor epimers **7x** and **7n** are 1.0 and 1.3, respectively.

***exo*-3-(Hydroxymethyl)tricyclo[5.3.0.0^{1,4}]decane (7x)**: ^{1}H NMR ($CDCl_3$) δ 1.0–2.4 (16 H), 3.5–3.7 (2 H, m); ^{1}H NMR (100 MHz) δ 1.0–1.3 (1 H), 1.3–2.4 (15 H), 3.5–3.7 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 67.9 (t, CH_2OH), 53.6 (s), 50.8 (d), 49.4 (d), 39.9 (t), 35.5 (d), 33.2 (t), 32.6 (t), 31.5 (t), 26.0 (t).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.37; H, 11.03.

***endo*-3-(Hydroxymethyl)tricyclo[5.3.0.0^{1,4}]decane (7n)**: ^{1}H NMR ($CDCl_3$) δ 0.8–2.8 (16 H), 3.6 (2 H, m); ^{1}H N (100 MHz) δ 1.0–1.3 (1 H, m), 1.3–2.3 (14 H), 2.3–2.8 (1 H, m), 3.51 (1 H, dd, J = 6.8, 10.6 Hz), 3.66 (1 H, dd, J = 8.3, 10.6 Hz); ^{13}C NMR ($CDCl_3$) δ 64.9 (t, CH_2OH), 54.5 (s), 41.1 (d), 46.6 (d), 38.5 (t), 34.7 (t), 32.5 (d), 32.3 (t), 31.9 (t), 36.5 (t), 25.1 (t).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.39; H, 10.93.

***exo*-[(3-Toluenesulfonyloxy)methyl]tricyclo[5.3.0.0^{1,4}]decane (43).** The alcohol **7x** (332 mg, 2 mmol), pyridine (2.4 mL), and *p*-toluenesulfonyl chloride (420 mg) were combined at 0 °C and treated analogously to the procedure described above for preparation of **18** (R = Ts) to afford crude tosylate **43** (423 mg, 66% yield) which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 0.9–2.1 (15 H), 2.44 (3 H, s), 4.00 (2 H, d, J = 5.4 Hz), 7.32 (2 H, d, J = 8 Hz), 7.77 (2 H, d, J = 8 Hz).

Tricyclo[6.3.0.0^{1,5}]undecane (8). The tosylate **43** (375 mg) in glacial acetic acid (50 mL) was boiled under reflux under dry nitrogen for 7 h. After the mixture cooled, water (140 mL) was added, and the mixture was extracted with pentane (3 × 110 mL). The pentane extract was washed with saturated aqueous $NaHCO_3$ and then saturated aqueous NaCl and dried ($MgSO_4$). Removal of solvent by rotary evaporation followed by preparative gas–liquid phase chromatography on a 3 ft × 0.25 in. column packed with 10% Dow Corning 710 silicone oil on 60/80 Chromosorb W at 100 °C afforded tricyclic olefin **44**: 47 mg (27% yield); ^{1}H NMR ($CDCl_3$) δ 1.0–2.2 (12 H), 2.4–2.6 (1 H, m), 2.6–2.9 (1 H), 5.48 (2 H, m); mass spectrum (70 eV), *m/e* (relative intensity) 39 (65), 40 (21), 41 (60), 51 (41), 52 (26), 55 (24), 63 (24), 65 (50), 66 (38), 67 (43), 77 (74), 78 (63), 79 (91), 80 (77), 81 (52), 91 (100), 92 (77), 93 (58), 94 (41), 103 (26), 105 (83), 106 (65), 107 (515), 115 (20), 117 (25), 119 (97), 120 (86), 121 (21), 133 (53), 148 (86), 149 (26). No attempt was made to optimize the yield of **44**. The olefin was characterized further by conversion of the symmetrical hydrocarbon **8**.

A solution of the tricyclic olefin **44** (54 mg) in methanol (1 mL) was stirred magnetically with 10% Pd/C (10 mg) under an atmosphere of hydrogen for 1 h during which hydrogen (8 mL) was absorbed by the solution. The catalyst was removed by filtration, and the solvent was removed by rotary evaporation. The residue was taken up in pentane, washed with water, and dried ($MgSO_4$). Rotary evaporation of solvent gave the title hydrocarbon **8**: 44 mg (80%); ^{13}C NMR ($CDCl_3$) δ 61.8 (s), 52.2 (d), 42.0 (t), 33.41 (t), 33.37 (t), 26.7 (t).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.87; H, 12.11.

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Registry No. 3b, 79618-34-1; **6**, 79618-35-2; **7x**, 79618-36-3; **7n**, 79646-87-0; **8**, 61950-20-7; **9**, 24731-17-7; **10** (R = H), 53544-46-0; **10** (R = Ts), 41825-83-6; **11**, 79618-37-4; **12**, 79618-38-5; **13**, 79618-39-6; **14**, 79618-40-9; **15**, 79618-41-0; **16**, 1120-80-5; **17**, 52358-10-8; **18** (R = H), 79618-42-1; **18** (R = Ts), 79618-43-2; **20**, 79618-44-3; **21a**, 16452-34-9; **21b**, 766-02-9; **22a**, 79618-45-4; **22b**, 21297-99-4; **23a**, 79618-46-5; **23b**, 79618-47-6; **31**, 79618-48-7; **34x**, 79646-88-1; **34n**, 79646-89-2; **36x**, 79618-49-8; **36n**, 79646-90-5; **43**, 79618-50-1; **44** (isomer 1), 79618-51-2; **44** (isomer 2), 79618-52-3; (1-cyclohexenyl)-methanol, 4845-04-9; (2-cyclopenten-1-yl)acetic acid, 13668-61-6; 1-carbethoxycyclopentene, 10267-94-4; α-ethoxyethyl propargyl ether, 18669-04-0; 2-[5-(α-ethoxyethoxy)-3-pentyn-1-yl)-1-methylenecyclopentane, 79618-53-4; 5-(2-cyclohexen-1-yl)-1-(α-ethoxyethoxy)-2-pentyne, 79618-54-5; 5-(2-cyclohexen-1-yl)-2-pentyn-1-ol, 79618-55-6; 5-(2-cyclopenten-1-yl)-1-(α-ethoxyethoxy)-2-pentyne, 79618-56-7; 5-(2-cyclopenten-1-yl)-2-pentyn-1-ol, 79618-57-8; CuOTf, 42152-44-3.