crystalline solid: mp 168-169 °C; NMR δ 1.22 (t, OCH_2CH_3, J = 7.5 Hz, 24 H), 4.2 (m, OCH_2CH_3, 16 H), 4.49 [t, $CH(CO_2Et)_2$, J = 7.0 Hz, 4 H], 4.96 (d, py CH_2, J = 7.0 Hz, 8 H), 7.22 (d, 3,5-py H, J = 7.5 Hz, 4 H), 7.58 (t, 4-py H, J = 7.5 Hz, 2 H); IR (KBr) 1725 (C=O) 1592, 1451, 1360, 1285, 1150, 1025 cm^{-1}. Anal. Calcd for $C_{42}H_{58}N_2O_{16}PdCl_2$: C, 49.25; H, 5.90; N, 2.73. Found: C, 49.08; H, 5.61; N, 2.51.

Fraction 2 was eluted with 30% methanol in ethyl acetate and upon concentration in vacuo afforded (12%) **8a** as yellow microcrystals: mp 185-190 °C; NMR δ 1.0 (t, OCH_2CH_3, J = 7.0 Hz, 24 H), 3.71-3.77 (2q, OCH_2^B, J = 7.0 Hz, 8 H), 3.85 (s, py CH_2, 8 H), 3.98-4.04 (2q, OCH_2^B, J = 7.0 Hz, 8 H), 7.13 (d, 3,5-py H, J = 8.0 Hz, 4 H), 7.45 (d, 3',5'-py H, J = 6.5 Hz, 4 H), 7.63 (t, 4-py H, J = 8.0 Hz, 2 H), 8.68 (d, 2',6'-py H, J = 6.5 Hz, 4 H); IR (KBr) 1673 (C=O), 1600, 1085 (C-O), 1050 cm^{-1}. Anal. Calcd for $C_{54}H_{62}N_4O_{16}Pd_2$: C, 52.48; H, 5.05; N, 4.53. Found: C, 52.30; H, 5.09; N, 4.44.

Complex 8b was synthesized in a similar manner from **3b**. Chromatography (ThLC) of the reaction mixture on silica gel eluting with 20% methanol in ethyl acetate afforded (40%) **8b** as yellow crystals: mp 236-238 °C; NMR δ 3.37 (s, OCH_3, 24 H), 3.82 (s, py CH_2, 8 H), 7.08 (d, 3,5-py H, J = 7.5 Hz, 4 H), 7.43 (d, 3',5'-py H, J = 6.5 Hz, 4 H), 7.60 (t, 4-py H, J = 7.5 Hz, 2 H), 8.55 (d, 2',6'-py H, J = 6.5 Hz, 4 H); IR (KBr) 1660 (C=O), 1422, 1282, 1172, 1062 cm^{-1}. Anal. Calcd for $C_{46}H_{46}N_4O_{16}Pd_2$: C, 49.17; H, 4.12; N, 4.98. Found: C, 49.33; H, 4.08; N, 4.81.

Photolysis of *trans*-7b. A degassed solution of *trans*-**7b** (50 mg) in methanol (200 mL) was photolyzed in the presence of benzil (10 mg) in a Pyrex vessel under argon for 8 h. The solvent was removed and the residue chromatographed (ThLC), eluting with 40% methanol in ethyl acetate, to give a slower moving fraction (R_f 0.28), which was identified as the yellow crystalline *cis*-**7b**: mp 224-225 °C; NMR δ 3.43 (s, OCH_3, 24 H), 3.81 (s, py CH_2, 8 H), 6.72 (s, olefinic H, 2 H), 7.07 (d, 3,5-py H, J = 8.0 Hz, 4 H), 7.20 (d, 3',5'-py H, J = 6.5 Hz, 4 H), 7.58 (t, 4-py H, J = 8.0 Hz, 2 H), 8.39 (d, 2',6'-py H, J = 6.5 Hz, 4 H); IR (KBr) [1720, 1680, 1650 (C=O)], 1180, 1070 (C-O), 846 cm^{-1}. Anal. Calcd for $C_{46}H_{48}N_4O_{16}Pd$: C, 49.08; H, 4.29; N, 4.97. Found: C, 49.19; H, 4.24; N, 4.74.

Catalytic Hydrogenation of 7b. A solution of **7b** (20 mg, 0.017 mmol) in methanol (50 mL) was hydrogenated in the presence of 5% Pd/C under 1 atm of hydrogen at 26 °C. After 1 equiv of hydrogen was consumed, the reaction was stopped by filtration of the catalyst. Upon concentration, the residue was shown to be the saturated complex **7d** as a yellow solid: mp 229-230 °C; 100%; NMR δ 3.01 [s, (py CH_2)$_2$, 4 H], 3.41 (s, OCH_3, 24 H), 3.87 (s, py CH_2, 8 H), 7.12 (d, 3,5-py H, J = 7.5 Hz, 4 H), 7.25 (d, 3',5'-py H, J = 6.0 Hz, 4 H), 7.64 (t, 4-py H, J = 7.5 Hz, 2 H), 8.45 (d, 2',6'-py H, J = 6.0 Hz, 4 H); IR (KBr) 1670 (b, C=O), 1618, 1170, 1060 (C-O), 835 cm^{-1}. Anal. Calcd for $C_{46}H_{50}N_4O_{16}Pd_2$: C, 48.99; H, 4.43; N, 4.96. Found: C, 49.04; H, 4.35; N, 4.68.

Selective Hydrogenation of 8b with Lindlar Catalyst. A solution of **8b** (20 mg, 0.017 mmol) in methanol (50 mL) was hydrogenated in the presence of Lindlar catalyst (10 mg) under 1 atm of hydrogen at 25 °C. After 1 equiv of hydrogen was consumed, the catalyst was removed by filtration. Upon concentration of the solvent, the yellow crystalline residue was shown to be identical with *cis*-**7b**: mp 224-225 °C, 15 mg (75%); NMR and IR spectra were superimposable with *trans* ⇄ *cis*-**7b** sample.

X-ray Data Collection. An orange crystal of dimensions 0.22 × 0.32 × 0.44 mm was mounted in random orientation on an Enraf-Nonius CAD-4 automatic diffractometer equipped with a graphite monochromator and Mo Kα radiation (λ = 0.71073 Å). Lattice constants and crystal orientation were determined from the setting angles of 25 precisely centered reflections having 40° ≤ 2θ ≤ 47°. The space group is $C2/c$ (by systematic absences hkl with $h + k$ odd, $h0l$ with l odd, and successful refinement in the centrosymmetric space group). Intensity data were collected by the θ-2θ scan method using variable scan rates designed to yield $I \simeq 25\sigma(I)$ for all observable reflections. Scan speeds, determined during a 10.0 deg min^{-1} prescan of each reflection, varied from 0.39 to 10.0 deg min^{-1}. Reflections having $I < \sigma(I)$ during the prescan were considered unobserved, and the maximum time spent on a weak reflection was limited to 120 s. Scan angles varied as $\Delta\theta = 0.5 + 0.35 \tan\theta$ and were extended at each extreme by 25% to provide background measurements. All data in one quadrant having 2° ≤ 2θ ≤ 50° were measured in this fashion. During data collection, two reflections were recentered every 200 measurements as a check of crystal orientation, and the intensities of three standards were remeasured periodically, but no significant changes were noted in either test.

During data reduction, Lorentz, polarization, and background corrections were applied. Empirical absorption corrections, based upon ψ scans of two reflections at $\chi \simeq 90°$ with differing θ values, were applied to the data; the minimum relative transmission factor was 92%. Of the 4226 unique data measured, 2964 had $I > 3\sigma(I)$ and were used in the structure solution and refinement.

Structure Solution and Refinement. The structure was solved by heavy-atom methods. Refinement was accomplished by full matrix least squares with unit weights. All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package programs. All nonhydrogen atoms were treated anisotropically; hydrogen atoms were placed in calculated positions with isotropic B = 4.0 Å^2 and were not refined. In calculation of H atom positions, the C-H distance was taken to be 0.95 Å, and a staggered configuration for ethyl groups was assumed. At convergence, R = 0.030 for 2964 data and 307 variables. A final difference map exhibited peaks of density less than 0.60 e Å^{-3}, associated with the Pd position, as its only significant features. Refined coordinates for nonhydrogen atoms are listed in Table IV.

Acknowledgment. We are grateful to the National Science Foundation and Dow Chemical USA for partial support of this work.

Registry No. 3a, 77502-99-9; **3b**, 80317-58-4; **4a**, 80327-86-2; **5a**, 80327-87-3; **5b**, 80327-88-4; **6a**, 80327-89-5; **7a**, 80327-90-8; **7b**, 80374-71-6; **7c**, 80327-91-9; **7d**, 80327-92-0; **8a**, 80327-93-1; **8b**, 80327-94-2; **9a**, 80327-95-3.

Supplementary Material Available: Anisotropic thermal parameters, assigned hydrogen atom coordinates, and structure factors (15 pages). Ordering information is given on any current masthead page.

Copper(I) Catalysis of Olefin Photoreactions. 9. Photobicyclization of α-, β-, and γ-Alkenylallyl Alcohols[1]

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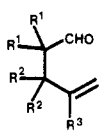
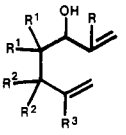
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received April 20, 1981*

Abstract: Cyclobutylcarbinyl alcohols of the bicyclo[3.2.0]heptane ring system are produced by UV irradiation of α-, β-, and γ-alkenylallyl alcohols in the presence of copper(I) trifluoromethanesulfonate (CuOTf). *endo*-2-Hydroxy epimers of bicyclo[3.2.0]heptan-2-ols are generated stereoselectively. This result as well as the effect of CuOTf on the ^{1}H NMR spectrum of 4,4-dimethyl-1,6-heptadien-3-ol suggests that coordination of two C=C bonds and the hydroxyl group with a single copper(I) is important. The derived bicyclo[3.2.0]heptan-2-ones fragment cleanly at 580 °C to afford cyclopent-2-en-1-ones. Geometric isomerization competes with photobicyclization of (*E*)- and (*Z*)-octa-2,7-dien-1-ols.

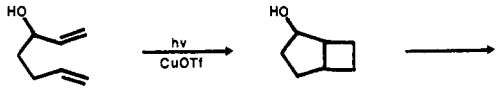
To enhance the utility of 2π + 2π photocycloadditions for organic synthesis, we are exploring copper(I)-catalyzed photochemistry[2] of olefins which bear functional substituents. Allylic substituents are of special interest since they can facilitate useful

0002-7863/82/1504-0998$01.25/0

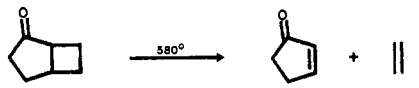
Table I. Synthesis of 3-Hydroxy-1,6-heptadienes 1

			Yield (%)
$R^1,R^2,R^3=H$	R=H	1a	73
$R^1,R^2,R^3=H$	R=Me	1b	82
$R^1=Me,R^2,R^3=H$	R=H	1c	86
$R^2=Me,R^1,R^3=H$	R=H	1d	67
$R^1=Me,R^2,R^3=H$	R=Me	1e	86
$R^1,R^2=H,R^3=Me$	R=Me	1f	83
$R^1,R^2=H,R^3=Me$	R=H	1g	88

transformations of the photoproducts involving cleavage of the cyclobutane ring. For example, photobicyclization of 1,6-heptadien-3-ols (**1**) in the presence of copper(I) trifluoromethane-



1 2

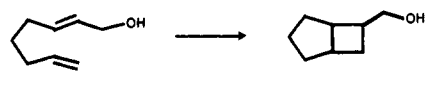


3 4

sulfonate (CuOTf) is a clean, high yield (81–91%) new method for synthesis of bicyclo[3.2.0]heptan-2-ols (**2**).[1] The cyclobutane ring of the ketones **3**, derived from the photoproducts **2**, fragments cleanly at 580 °C to afford cyclopent-2-enones (**4**). The overall process, **1** → **4**, provides the first example of a novel stepwise olefin metathesis approach of cycloalkene synthesis.

Our success in achieving photobicyclization of α-alkenylallyl alcohols such as **1** led us to explore the feasibility of related bicyclizations of β- and γ-alkenylallyl alcohols. We now report that β-(4-pentenyl)allyl alcohol **5a** produces **6** and γ-(4-pentenyl)allyl alcohol **7** produces **8** upon UV irradiation in the presence of CuOTf as a catalyst. Furthermore, in a forthcoming paper such photobicyclizations are shown to be of value for construction of a variety of polycyclic cyclobutanes including complex multicyclic carbon networks which are not readily available by other synthetic methods.[1b]

5a 6

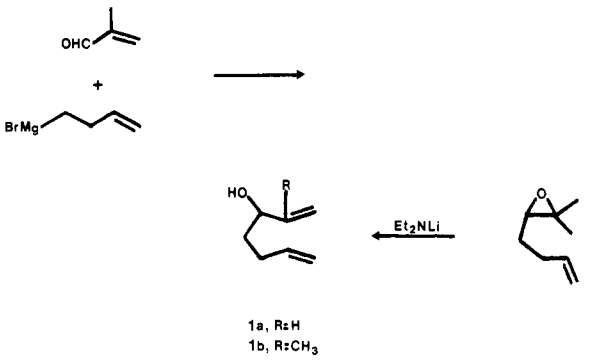


7 8

Some mechanistic details of copper-catalyzed photobicyclizations were also explored in the present study. The nature of the diene–copper interaction was considered for one photobicyclization substrate. The role of copper–oxygen interactions in promoting stereoselection during bicyclization was also examined.

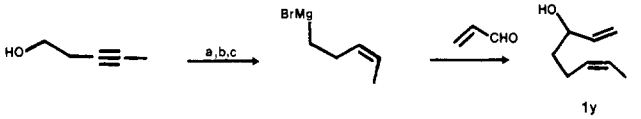
Results and Discussion

A. Synthesis of Photobicyclization Substrates. 3-Hydroxy-1,6-heptadienes (1). A variety of potentially general routes are known for synthesis of 3-hydroxy-1,6-heptadienes. Thus, 1,2 addition of Grignard reagents from 4-halo-1-butenes to acrolein or methacrolein[3] affords **1a** or **1b**. We used this approach to



1a, R=H
1b, R=CH_3

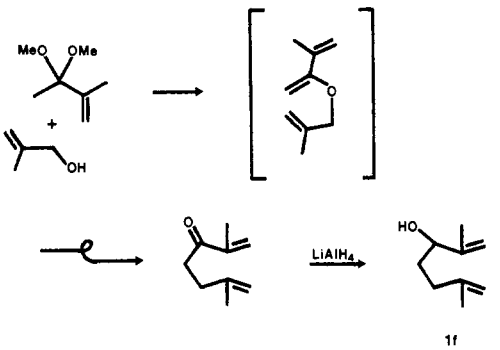
prepare 3-hydroxy-1,6-octadiene (**1y**) stereospecifically from



a) H_2/Pd $BaCO_3$/quinoline, b) PBr_3, c) Mg

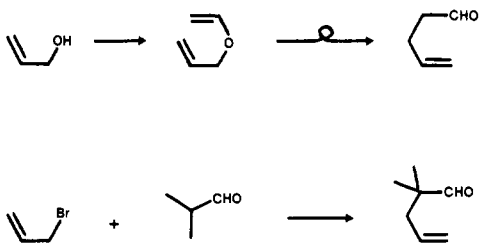
3-butyn-1-ol. Regioselective β elimination of an epoxide also provides **1b**.[4]

Carbon–carbon bond formation between allyl alcohols and carbonyl compounds via Claisen rearrangement of allyl vinyl ethers provides precursors to the requisite hydroxydienes. Thus, methallyl alcohol affords **1f** after hydride reduction of an intermediate



1f

1,6-heptadien-3-one.[5] Pent-4-enals are readily available in good yields from allyl alcohols by Claisen rearrangement of allyl vinyl ether intermediates.[6] Direct alkylation of aldehydes[7] or of the



(1) (a) For previous papers in this series and a preliminary account of some of the present work, see: Salomon, R. G.; Coughlin, D. J.; Easler, E. M. *J. Am. Chem. Soc.* **1979**, *101*, 3961–3 and references cited therein. (b) Salomon, R. G.; Ghosh, S.; Zagorski, M. G.; Reitz, M. *J. Org. Chem.*, in press.

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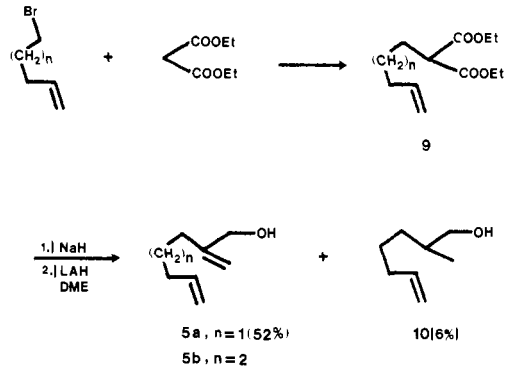
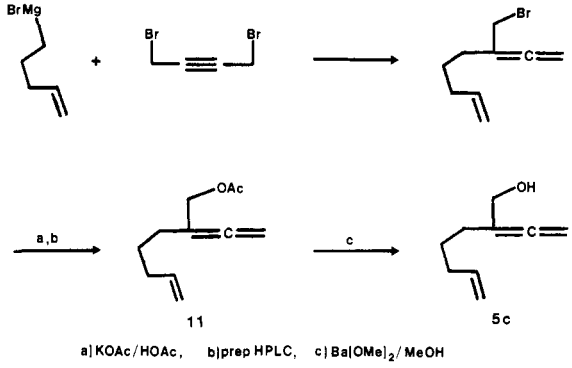
Scheme I



Scheme II



derived imines[8] with allylic halides also provides 4-pentenals. Reaction of 2,2-dimethyl-4-pentenal with vinylmagnesium chloride affords **1c**.[9] We used the analogous reactions of vinylmagnesium bromide or 2-propenylmagnesium bromide with 4-pentenals to prepare **1a-g** (Table I). Similar reaction of allylacetone with vinylmagnesium bromide affords 3-hydroxy-3-methyl-1,6-heptadiene (**1h**).[10]

2-(Hydroxymethyl)-1,6-heptadiene (5a) and 2-(Hydroxymethyl)-1,7-octadiene (5b). Vigorous hydride reduction of the sodium enolate of diethyl alkylmalonates is an excellent method for synthesis of 2-substituted allyl alcohols.[11] It is especially well suited to the synthesis of photobicyclization substrates since overreduction products (e.g. **10**) do not interfere with photobicyclization. Thus, diethyl 4-pentenylmalonate (**9**) is obtained by alkylation of dimethyl malonate. Reduction of the sodium enolate from **9** with $LiAlH_4$ in boiling 1,2-dimethoxyethane (glyme) affords a 9:1 mixture of **5a** and **10** (Scheme I). A related substrate, 2-(hydroxymethyl)-1,7-octadiene (**5b**), is available by an analogous synthesis from 6-bromo-1-hexene. A substrate incorporating an allene group was prepared as outlined in Scheme II. Coupling of 4-penten-1-ylmagnesium bromide with 1,4-dibromo-2-butyne produces a bromoallene. Acetoylis of the crude bromide followed by distillation and preparative high-pressure liquid chromatography provides the corresponding acetoxyallene (**11**). Deacetylation by transesterification with $Ba(OMe)_2$ as catalyst delivers 3-(hydroxymethyl)-1,2,7-octatriene (**5c**).

Octa-2,7-dien-1-ol (7). Alkylation of 3-(α-ethoxyethoxy)-1-lithiopropyne with 5-bromo-1-pentene and removal of the α-ethoxyethyl protecting group with aqueous acid readily affords

Scheme III

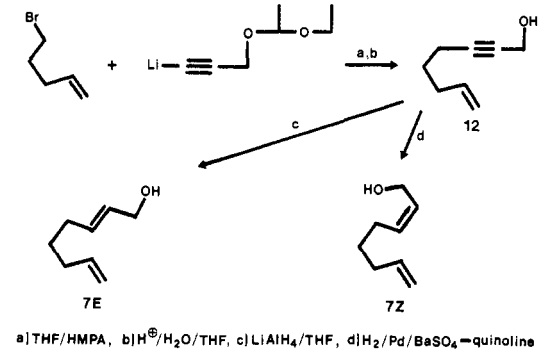
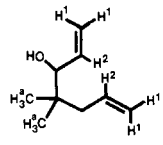
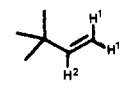
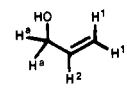


Table II. $\Delta\delta$ for Various Proton Resonances of Olefins in the Presence of CuOTf or $CuClO_4$

Olefin	Hydrogen	$\Delta\delta$	Cu salt
	H^a	+0.2	
	H^1	−0.4 to −0.5	CuOTf
	H^2	0 to +0.2	
	H^1	−0.4	CuOTf[15]
	H^2	−0.2	
	H^a	+0.2	
	H^1	−0.8	$CuClO_4$[16]
	H^2	−0.8	

oct-7-en-2-yn-1-ol (**12**) in 82% yield overall. Reduction of **12** with $LiAlH_4$ produces the *E* isomer **7E** stereoselectively as expected.[12] Hydrogenation of **12** in the presence of palladium on $BaSO_4$ and an equal weight of quinoline produces the *Z* isomer **7Z** stereoselectively as expected (Scheme III).[13]

B. Interaction of CuOTf with 4,4-Dimethyl-1,6-heptadien-3-ol (1c). Previous studies on the ^1H NMR spectra of olefins in the presence of copper(I) trifluoromethanesulfonate (CuOTf)[14] or $CuClO_4$[15] showed that the chemical shifts of particular types of hydrogens experience changes ($\Delta\delta$) owing to complexation. If free olefin ligand and various mono and poly ligand complexes with copper(I) are present together in solution, the observed spectrum is a weighted average since equilibration is rapid on the NMR time scale.[14] For copper(I)–olefin complexes, the chemical shifts of nonvinyl protons are sometimes shifted downfield ($\Delta\delta > 0$), but the chemical shifts of vinyl protons may be shifted either up- or downfield. Complexes with monodentate olefin ligands generally exhibit $\Delta\delta < 0$, whereas chelating multidentate complexes formed by some polyenes exhibit $\Delta\delta > 0$. The $\Delta\delta$ observed for various hydrogens in the NMR spectrum of **1c** in the presence of 1 equiv of CuOTf are useful (Table II). Both up- and downfield shifts are found for the vinyl proton resonances. This contrasts with the exclusively upfield shifts of the vinyl proton resonances found for 3,3-dimethyl-1-butene upon coordination with CuOTf[14] or for allyl alcohol upon coordination with $CuClO_4$.[15] Shielding of vinyl protons may indicate a preponderance of metal to ligand electron transfer by π back-bonding over ligand to metal electron transfer by σ donation. This is typical of Cu(I)

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(11) (a) Marshall, J. A.; Cohen, N.f Hochstetler, A. R. *J. Am. Chem. Soc.* **1966**, *88*, 3408–17. (b) Marshall, J. A.; Andersen, N. H.; Hochstetler, A. R. *J. Org. Chem.* **1967**, *32*, 113–8.

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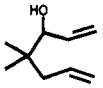
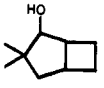
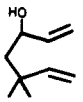
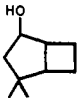
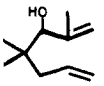
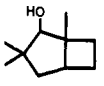
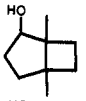
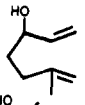
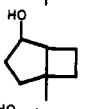
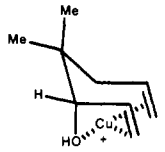
Table III. Photobicyclization of 1,6-Heptadien-3-ols

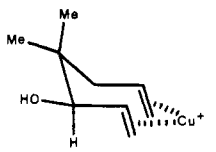
Entry	Diene 1	Hydroxybicyclo-alkane 2	Yield [%]	endo:exo
a			86	9:1
b			81	6:1
c			91	9:1
d			84	3:4
e			83	3:2[a]
f			c	>20:1[b]
g			78	5:1
h			89	>20:1[b]

[a] See text. [b] Only one epimer detected by ^{1}H NMR. [c] 40% conversion after 24 h.

complexes of cis coordinated bridged polyene complexes.[14] This behavior of the ^{1}H NMR spectrum of **1c** in the presence of CuOTf suggests that at least some of this diene must be coordinated with copper(I) as a bidentate chelating ligand as, for example, in **1cn** or **1cx**. A preference of **1cn** is also indicated by the stereochemical



1cn



1cx

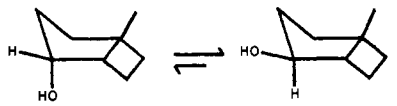
course of the photobicyclization of **1c** in the presence of CuOTf as catalyst (vide infra).

C. Photobicyclizations. 1,6-Heptadien-3-ols 1. UV irradiation of 1,6-heptadien-3-ols **1** in the presence of CuOTf in Et_2O solution results in a clean photobicyclization reaction to afford 3-hydroxybicyclo[3.2.0]heptanes (**2**) in high yields (Table III). Structures were assigned to products **2a**, **2b** and **2g** by comparison of their ^{1}H NMR spectra with data reported previously for the endo and exo epimeric isomers of each alcohol.[16,17] The proton α to the hydroxyl group appears as a "quartet" with $J \simeq 8$ Hz for the endo epimers and as a doublet with $J \simeq 4$ Hz for the exo epimers in the ^{1}H NMR spectra of **2a** and **2g**. The ^{1}H NMR spectra of the major epimer of **2c** from photobicyclization of **1c** exhibits a doublet with $J = 6.7$ Hz while the minor epimer shows a doublet with $J = 4.6$ Hz for the C-2 proton. On this basis we assign an endo configuration to the C-2 hydroxyl in major epimer and an exo configuration to the minor epimer. In contrast, the major epimer of **2d** from photobicyclization of **1d** exhibits a doublet with $J = 5$ Hz while the minor epimer shows a quartet with $J = 8$ Hz for the C-2 proton. In close analogy to the epimers of **2a** and **2g**, we assign an exo configuration to the C-2 hydroxyl in the major epimer and an endo configuration to the minor epimer. Additional support for this assignment was obtained by reduction of the corresponding ketone **3d** with $NaBH_4$ in ethanol. As expected[16,17] hydride deliverly occurs predominately from the least congested convex side of the molecule to afford a 4:1 mixture respectively of endo and exo epimeric alcohols.

The ^{1}H NMR spectrum of the photobicyclization product **2e** clearly indicates a 3:2 mixture of the C-2 epimers. We did not separate the mixture. Nevertheless, it is apparent that the major epimer is characterized by a singlet at δ 3.69 (1 H) and three singlets at δ 0.97 (3 H), 1.10 (3 H), and 1.28 (3 H), while the minor isomer exhibits a singlet at δ 3.32 (1 H) and two singlets at δ 0.87 (3 H) and 1.15 (6 H). Reduction of the corresponding ketone **3e** affords a 1:3 mixture in which the epimer with a ^{1}H NMR singlet at δ 3.32 is now predominant. This suggests that the latter is the endo isomer. However, we are reluctant to make an assignment of stereochemistry at C-2 on the basis of this result alone.

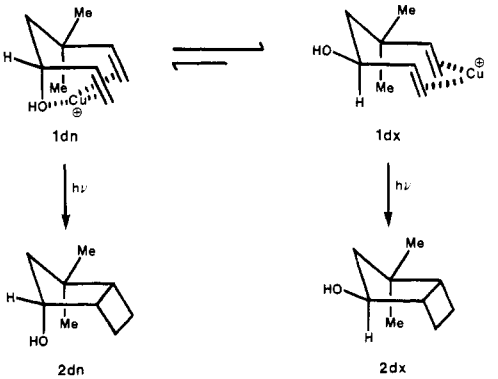
Since the ^{1}H NMR spectrum of the photobicyclization product from **1f** exhibits only two singlets for methyl group proton resonances, we assume that **2f** is the endo C-2 epimer in analogy with photobicyclizations of **1a–c**. Similarly, the ^{1}H NMR spectrum of the photobicyclization product from **1h** exhibits only one singlet for methyl group proton resonances, and we assume that **2h** is the endo-2-hydroxy epimer.

The stereoselectively of these photobicyclizations is noteworthy (Table III). With the important exception of **1d** → **2d**, there is often a great preference for generation of the endo epimer. This epimer is generally thermodynamically the least stable because the hydroxyl substitutent occupies a pseudoaxial configuration. Thus, the endo epimer **2gn** is transformed into the exo epimer **2gx**



2gn 2gx

upon heating in the presence of aluminum isopropoxide and a trace of acetone.[16] After 24 h in boiling toluene, a mixture containing endo and exo epimers in a ratio of 1:2 is produced.[16] The predominant generation of endo epimers during photobicyclization is expected if the substrate preferentially acts as a tridentate ligand as in **1cn** rather than a bidentate ligand as in **1cx**. The preferential formation of **2dx** from **1d** is the exception which proves the rule. In this case, one of the methyl substituents must occupy a pseudoaxial endo configuration which favors **1dx** over **1dn**.



1dn 1dx

2dn 2dx

Photobicyclization of 4-hydroxy-1,6-heptadiene in the presence of CuOTf as catalyst is nonstereoselective.[18] For tridentate

(16) Gassman, P. G. Pascone, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 7801–7813.

(17) Svensson, T. *Chem. Scr.* **1973**, *3*, 171–5.

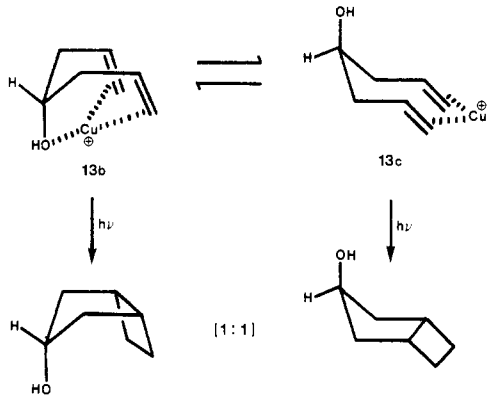
(18) Evers, J. Th. M.; Mackor, T. *Tetrahedron Lett.* **1978**, *821–4*.

Table IV. Synthesis of Cyclopentenones from 3-Hydroxy-1,6-heptadienes

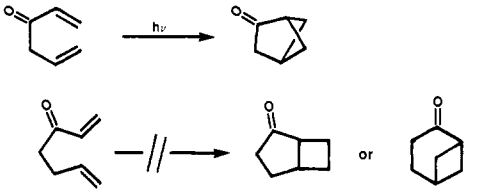
ENTRY	HYDROXYDIENE 1 (% yield)*	BICYCLOHEPTANOL 2 (% yield)*	BICYCLOHEPTANONE 3 (% yield)*	CYCLOPENTENONE 4 (% yield)*
a	 (73)	 (86)	 (78)	 (70)
b	 (82)	 (81)	 (67)	 (72)
c	 (86)	 (91)	 (92)	 (78)
d	 (67)	 (84)	 (92)	 (87)
e	 (86)	 (83)	 (93)	 (54)

*Yields are of pure products isolated by distillation.

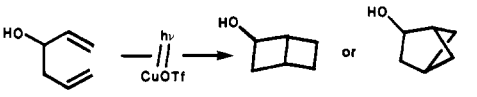
coordination of this hydroxydiene ligand with Cu(I) to be achieved a boat-like conformation, as in **13b**, must be adopted. Apparently there is no preference for **13b** over alternative bidentate coordination as in the chair-like arrangement **13c**.



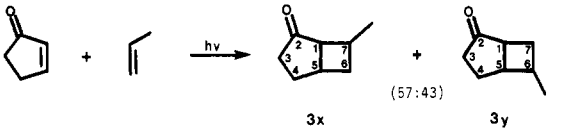
Photobicyclization provides an effective new route for synthesis of bicyclo[3.2.0]heptan-2-ols. One previous approach which affords mainly the exo-hydroxyl isomer involves solvolytic rearrangement of bicyclo[2.2.1]hept-2-en-7-ol followed by catalytic hydrogenation.[19] Endo isomers are the predominant products from reduction of the corresponding ketones **3** with $LiAlH_4$.[17] The only previous *general* route for synthesis of the requisite bicyclo[3.2.0]heptan-2-ones **3** involves $2\pi + 2\pi$ photocycloaddition of cyclopent-2-en-1-ones with olefins.[16,17,20,21] Of course this approach is limited by the availability of the requsite cyclopentenones and has no value for synthesis of cyclopentenones by stepwise olefin metathesis (vide infra). Copper-catalyzed photobicyclization provides a topologically different route to the bicyclo[3.2.0]heptane skeleton. This approach often provides the method of choice for elaboration of bicyclo[3.2.0]heptan-2-ones **3** which are versatile intermediates in organic synthesis.[22] Thus, photobicyclization followed by oxidation provides bicyclic ketones **3** from acyclic alcohols **1** in 45-72% overall yields (**Table** IV). It should be noted in this context that whereas direct irradiation of 1,5-hexadien-3-one gives bicyclo[2.1.1]hexan-2-one in fair yield,[23]

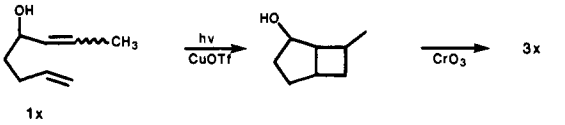


direct irradiation of the homologous 1,6-heptadien-3-one does not result in photobicyclization, only polymer being formed.[24] The success of the **1** → **2** conversion also contrasts with the reported failure of 1,5-hexadien-3-ol to undergo photobicyclization in the presence of CuOTf.[18]

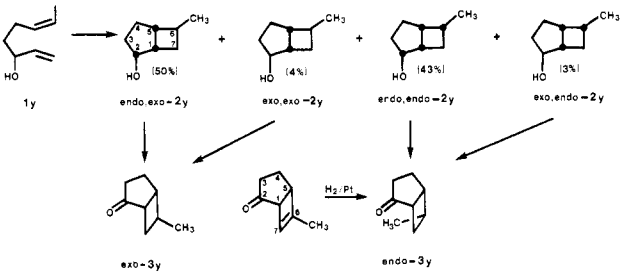


The structural specificity of the photobicyclization route to bicyclo[3.2.0]heptan-2-ones will certainly find synthetic applications. Thus, whereas photocycloaddition of propene with cyclopentenone affords a mixture of structural isomers **3x** and **3y**,





photobicyclization of **1x** followed by oxidation necessarily affords **3x** exclusively.[25] A similar sequence leads to a 1:1 mixture of C-6 epimers of **3y** starting from the pure *Z* isomer of **1y**. Thus,



UV irradiation of *Z*-**1y** in the presence of CuOTf affords a mixture of stereoisomeric 2-hydroxy-6-methylbicyclo[3.2.0]heptanes. The structures of *exo*- and *endo*-**3y** were established by ^1H and ^{13}C NMR spectral comparison with samples prepared in a previous study[25] (see Experimental Section). In that study the endo orientation of the methyl group in the *endo*-**3y** were demonstrated by preparing this isomer from 6-methylbicyclo[3.2.0]hept-6-en-2-one by catalytic hydrogenation which is expected to involve deliverly of hydrogen to the convex exo face of the olefin. Although none of the isomeric alcohols **2y** were isolated completely

(19) Winstein, S.; Stafford, E. T. *J. Am. Chem. Soc.* **1957**, *79*, 505–6. Winstein, S.; Gradient, F.; Stafford, E. T.; Klinedinst, P. E., Jr. *Ibid.* **1958**, *80*, 5895–6.

(20) For reviews, see the following: (a) Eaton, P. E. *Acc. Chem. Res.* **1968**, *1*, 50. (b) Bauslaugh, P. G. *Synthesis* **1970**, *287*–300. (c) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41.

(21) (a) Corey, E. J.; Bass, J. D.; Le Mahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *88*, 5570 and references cited therein. (b) House, H. O.; Cronin, T. H. *J. Org. Chem.* **1965**, *30*, 1061. (c) Nelson, P. J.; Osterm, D.; Lassila, J. D.; Chapman, O. L. *Ibid.* **1969**, *34*, 811. (d) Eaton, P. E. *J. Am. Chem. Soc.* **1952**, *84*, 2454. (e) Criegee, R.; Furrer, H. *Chem. Ber.* **1964**, *97*, 2949. (f) Eaton, P. E. *Tetrahedron Lett.* **1964**, *3695*. (g) Cargill, R. L.; Damewood, J. R.; Cooper, M. M. *J. Am. Chem. Soc.* **1966**, *88*, 1330. (h) Cantrell, T. S.; Solomon, J. S. *Ibid.* **1970**, *92*, 4656–63. (i) Cargill, R. L.; Wright, B. W. *J. Org. Chem.* **1975**, *40*, 120–22.

(22) Ali, S. M.; Lee, T. V.; Roberts, S. M. *Synthesis* **1977**, 155–66.

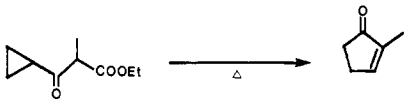
(23) Bond, F. T.; Jones, H. L.; Scerbo, L. *Tetrahedron Lett.* **1965**, 4685–6.

(24) See: Srinivasan, R., Ed. "Organic Photochemical Syntheses"; Wiley: New York, 1971; Vol. 1, p 35.

(25) Shih, C.; Fritzen, E. L.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 4462–71.

pure, their structures could be assigned by correlation with the ketones **3y**. Thus, *endo,exo*-**2y**, and *exo,exo*-**2y** were isolated as a mixture which afforded pure *exo*-**3y** upon oxidation. No trace of *endo*-**3y** was generated from this oxidation in accord with the conclusion that these alcohols are epimeric at C-2. The major epimer is assumed to be the endo-hydroxy isomer in analogy with the preferential formation of endo isomers shown above (see Table III). Similary, *endo,endo*-**2y** and *exo,endo*-**2y** were isolated as a mixture which afforded pure *endo*-**3y** upon oxidation. Again, the major epimer *endo,endo*-**2y** is assumed by analogy to be the endo-hydroxy isomer. Photobicyclization of **1y** is thus stereoselective with respect to configuration α to the hydroxyl substituent and, necessarily, structurally specific with regard to the position of attachment of the methyl substituent. However, this photobicyclization is not at all stereospecific with respect to configuration α to the methyl substituent. Further discussion of this latter point is deferred to a subsequent section.

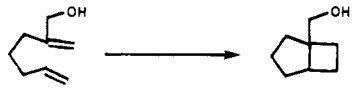
We demonstrated a new synthetic application of bicyclo[3.2.0]heptan-2-one intermediates. Thus, Jones oxidation of **2** provides ketones **3** which fragment cleanly at 580 °C to afford cyclopent-2-en-1-ones **4** (Table IV) with ethylene as the sole byproduct.[1] The 72% yield obtained in the **3b** → **4b** pyrolytic conversion compares favorably with the previous synthesis of **4b** by pyrolysis of **14**.[26] The cyclopentenone **4b** is also available in



14 4b

lower yields from 2-methylcyclopentane-1,3-dione (51%),[27] ethyl 2-cyclopentanonecarboxylate (43%),[16] or 1-methylcyclopentene (24%).[28] 5,5-Dimethylcyclopent-2-en-1-one (**4c**) is an important synthon for sesquiterpenes such as the antitumor agents, illudin M[29] and coriolin,[30] as well as an alkaloid from tobacco.[31] Copper-catalyzed photobicyclization of the readily available diene **1c** in conjunction with Jones oxidation and pyrolysis is probably the method of choice for synthesis of **4c**. The 65% overall yield of the **1c** → **4c** conversion compares favorably with synthesis of **4c** from 2,2-dimethylcyclopentanone (60%)[29c] or 2,2-dimethylpent-4-enoic acid (40%).[32]

β-(4-Pentenyl)allyl Alcohols (2-(Hydroxymethyl)-1,6-heptadienes). The efficient photobicyclizations of α-butenylallyl alcohols described in the previous section led us to examine the feasibility of analogous cyclization of β- and γ-(4-pentenyl)allyl alcohols. A sample of 2-(hydroxymethyl)-1,6-heptadiene (**5a**) containing

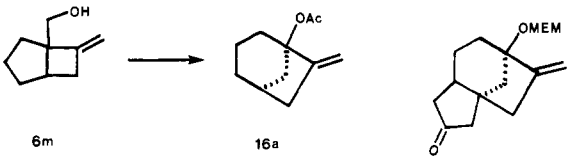


5a 6

10% of 2-methylhept-6-en-1-ol (**10**) was irradiated in the presence of CuOTf as catalyst. A mixture containing 1-(hydroxymethyl)bicyclo[3.2.0]heptane (**6**) and unreacted **10** was obtained in virtually quantitative yield. The bicyclic alcohol **6** is readily separated from **10** by gas–liquid phase chromatography (GLPC). For preparative purposes, selective destruction, of **10**, e.g., with $KMnO_4$, can be envisioned for facile purification of **6**. Assignment of structure **6** rather than the more symmetrical structure **15** to the photoproduct is supported by its ^{13}C NMR spectrum which shows eight magnetically nonequivalent carbons (see Experimental Section).

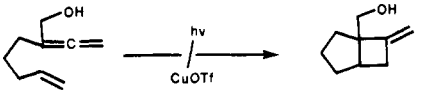
15

Ziegler demonstrated the feasibility of a solvolytic ring expansion route to 1-acetoxy-7-methylenebicyclo[3.2.1]octane (**16a**)



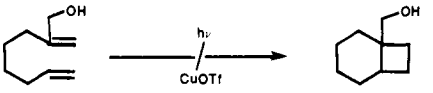
6m 16a 16b

from 1-(hydroxymethyl)-7-methylenebicyclo[3.2.0]heptane (**6m**).[33] The carbon network of **16** is ubiquitous in terpenoid natural products such as zizaene, steviol, cafestol, garryine, veatchine, garryfoline, and gibberellic acids. Gibberellic acid A_3 also has a hydroxyl substituent at the bridgehead corresponding to the acetoxy group in **16a**, and synthon **16b** has been used extensively in total synthesis.[34] Therefore we examined the feasibility of a direct photobicyclization route to **6m**. Irradiation of allene **5c** in the presence of CuOTf under conditions which efficiently transformed **5a** into **6** failed to induce any reaction.



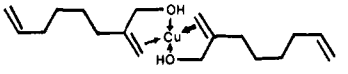
5c 6m

The photocycloadditions of allylic alcohols which we uncovered are remarkable in view of the proclivity of allyl alcohol toward photoinduced nucleophilic substitution which is also catalyzed by copper(I).[18] In contrast with the efficient photobicyclization **5a** to **6**, no analogous product, **17**, could be isolated from irradiation



5b 17

of the homologous 2-(hydroxymethyl)-1,7-octadiene (**5b**) in the presence of CuOTf. Rather, the major product is dimeric with vinyl groups intact. We interpret the dichotomy in the photochemistry of **5a** and **5b** in terms of the relative effectiveness of these two hydroxydienes as chelating ligands. *Photobicyclization requires coordination of both C=C bonds with the copper(I) catalyst.* This is readily achieved for **5a** but less readily for **5b** which may prefer to form a 2:1 complex, **18**. On the other hand,



18

there is no reason to expect that photoinduced reactions of the allylic alcohol moiety of **5b** such as nucleophilic displacement of an allylic hydroxy would require participation of the remote C=C

(26) Berkowitz, W. F.; Ozorio, A. A. *J. Org. Chem.* **1971**, *36*, 3787–92.
(27) Clark, R. D.; Heathcock, C. H. *J. Org. Chem.* **1973**, *38*, 3658.
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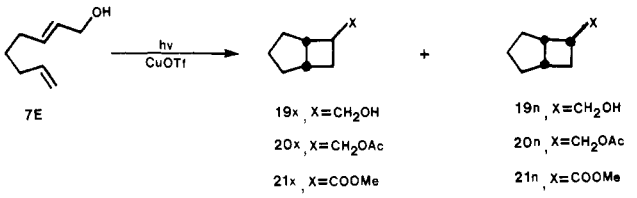
Table V. Photobicyclization of *Z* and *E* Dienes

diene	% of product 19x	19n
7E	76	24
7Z	51	49

bond in **5b**. UV irradiation of allyl alcohol in the presence of CuOTf is known to produce diallyl ether.[18]

γ-(4-Pentenyl)allyl Alcohols. Photocycloaddition of (*E*)-octa-2,7-diene-1-ol (*7E*) in the presence of CuOTf as a catalyst



7E

19x, X=CH_2OH 19n, X=CH_2OH

20x, X=CH_2OAc 20n, X=CH_2OAc

21x, X=COOMe 21n, X=COOMe

produces a mixture of *exo*-6-(hydroxymethyl)bicyclo[3.2.0]heptane (**19x**) and the endo epimer **19n** in 3:1 ratio, respectively. These isomers were readily separable by gas–liquid phase chromatography after conversion to the corresponding acetates **20**. The pure alcohols were then regenerated by treatment of the acetates with $Ba(OMe)_2$ in anhydrous methanol. The stereochemistries of the epimeric alcohols **19** were assigned by conversion to the corresponding methyl esters **21**. The ^1H NMR spectrum of **21n** features a one proton multiplet at δ 3.0–3.4 while **21x** has no resonance in this region. The spectrum of the major isomer agrees with that reported previously for *exo*-6-(carbomethoxy)bicyclo[3.2.0]heptane. The assignment of an exo stereochemistry to the carbomethoxyl in **21x** was based on the failure of this isomer to epimerize upon exposure to methoxide in boiling anhydrous methanol.[35] We checked the implicit assumption of this argument by examining the behavior of **21n**. As expected, the endo isomer **21n** epimerizes to the exo isomer **21x** upon exposure to methoxide in boiling anhydrous methanol.

Thus, as in the photobicyclization of **1y** described above, photobicyclization of **7E** is not stereospecific. This might have been expected since it is known that copper(I) catalyzes cis–trans isomerization of olefins.[36] On the other hand, photobicyclization of (*Z*)-octa-2,7-diene-1-ol (*7Z*) generated a relatively greater proportion of **19n** (see Table V). These photobicyclizations are not entirely stereorandom.

Summary

Copper(I)-catalyzed photobicyclization is a widely applicable, clean, high yield method for synthesis of bicyclo[3.2.0]heptanes with cyclobutylcarbinyl hydroxyl functionality. Bicyclo[3.2.0]-heptan-2-ones are obtained from the 2-hydroxylated photoproducts by oxidation. This two-step synthesis of bicyclo[3.2.0]heptan-2-ones is superior to a previous synthesis involving intermolecular photocycloaddition to cyclopentenones because the intermolecular route produces structural isomers. Furthermore, while the intermolecular route is limited by the availability of the requisite cyclopentenones, the intramolecular route actually provides a novel synthesis of cyclopentenones by thermal fragmentation of bicyclo[3.2.0]heptan-2-ones.

Experimental Section

General Data. Small scale irradiations (15–50 mL) were conducted in cylindrical quartz vessels which were cooled with an internal water-cooled cold finger. The reaction mixtures were stirred magnetically and irradiated externally with a Rayonet photochemical reactor (Southern New England Ultraviolet Co. Model RPR-100) with 254-nm lamps. Large scale irradiations (0.1–1.0 L) were conducted under dry nitrogen in cylindrical Pyrex vessels with a quartz water-cooled double-walled immersion well. The reaction mixtures were stirred magnetically and irradiated internally with a Hanovia medium-pressure 450-W mercury vapor lamp. Preparative gas–liquid phase chromatography was performed with a Varian Model 3700 instrument. Proton magnetic resonance spectra were recorded with a Varian A60A or XL-100 spectrometer with tetramethylsilane as internal standard. Carbon magnetic resonance spectra were reocorded with a Varian XL-100 spectrometer with tetramethylsilane as internal standard and multiplicities refer to ^{13}C–^1H coupled spectra. Microanalyses were performed by chemalytics, Inc., Tempe, AZ, and Spang Microanalytical Laboratories, Eagle Harbor, MI.

Materials. Diethyl ether solvent for photolyses was freshly distilled from lithium aluminum hydride under dry nitrogen immediately before use. Tetrahydrofuran (THF) was distilled under dry nitrogen from potassium benzophenone ketyl. Pent-4-enal,[6b] 2,2-dimethyl-4-pentenal,[6a] 3,3-dimethyl-4-pentenal,[6c] 4-methyl-4-pentenal,[6b] 4,4-dimethyl-3-hydroxy-1,6-heptadiene,[9] and $(CuOTf)_2 \cdot C_6H_6$[14] were prepared by reported procedures.

3-Hydroxy-1,6-heptadienes (1). Variously substituted hydroxyheptadienes **1** were prepared by analogy with the reported synthesis[9] of **1c** by reaction of vinylmagnesium bromide or 2-propenylmagnesium bromide in THF with variously substituted 4-pentenals or with allylacetone. Yields are listed in Table I.

1,6-Heptadien-3-ol (1a): bp 55–56 °C (12 mm); ^1H NMR (CCl_4) δ 1.3–1.8 (2 H), 1.9–2.3 (3 H), 4.04 (H, q, *J* = 6 Hz), 4.7–5.3 (4 H), 5.4–6.2 (2 H).

Anal. ($C_7H_{12}O$): C, H.

2-Methyl-1,6-heptadien-3-ol (1b): bp 65–70 °C (15 mm); ^1H NMR (CCl_4) δ 1.3–2.3 (8 H), 2.50 (H, s), 4.01 (H, t, *J* = 6 Hz), 4.7–5.3 (4 H), 5.5–6.2 (H, m).

Anal. ($C_8H_{14}O$): C, H.

4,4-Dimethyl-1,6-heptadien-3-ol (1c): bp 67–69 °C (12 mm); ^1H NMR ($CDCl_3$) δ 0.90 (6 H,s), 1.74 (H, s), 2.08 (2 H, d, *J* = 8 Hz), 3.85 (H, d, J = 6 Hz), 4.8–5.5 (4 H), 5.6–6.3 (2 H).

Anal. ($C_9H_{16}O$): C, H.

5,5-Dimethyl-1,6-heptadien-3-ol (1d): bp 73–76 °C (12 mm); ^1H NMR CCl_4) δ 1.05 (6 H, s), 1.4–1.6 (2 H), 2.11 (H, s), 4.10 (H, q, *J* = 5.5 Hz), 4.7–5.3 (4 H), 5.5–6.2 (2 H).

Anal. ($C_9H_{16}O$): C, H.

2,4,4-Trimethyl-1,6-heptadien-3-ol (1e): bp 89–91 °C (14 mm); ^1H NMR (CCl_4) δ 0.85 (3, H, s), 0.90 (3 H, s), 1.55 (H, s), 1.78 (3 H, br s), 2.2 (2 H, m), 3.83 (H, s), 4.8–5.3 (4 H), 5.5–6.2 (H, m).

Anal. ($C_{10}H_{18}O$): C, H.

2,6-Dimethyl-1,6-heptadien-3-ol (1f): bp 85–88 °C (12 mm); ^1H NMR (CCl_4) δ 1.5–2.3 (11 H), 3.97 (H, t, *J* = 6 Hz), 4.6–6,0 (4 H, m).

Anal. ($C_9H_{16}O$): C, H.

6-Methyl-1,6-heptadien-3-ol (1g): bp 76–77 °C (12 mm); ^1H NMR (CCl_4) δ 1.3–1.8 (5 H), 1.8–2.2 (2 H), 3.16 (H, s), 3.98 (H, q, *J* = 6 Hz), 4.65 (2 H, s), 4.8–5.3 (2 H), 5.81 (H, ddd, *J* = 5.5, 9.5, 17 Hz).

Anal. ($C_8H_{14}O$): C, H.

3-Methyl-1,6-heptadien-3-ol (1h): bp 55–56 °C (86% yield) (12 mm); ^1H NMR ($CDCl_3$) δ 1.27 (3 H, s), 1.4–1.8 (2 H, m), 1.83 (H, s), 1.9–2.4 (2 H, m).

Anal. ($C_8H_{14}O$): C, H.

(*Z*)-1,6-Octadien-3-ol (1y). This hydroxydiene was prepared stereospecifically from 3-pentyn-1-ol (8.1 g, 96 mmol) which was added to a suspension of 5% Pd on $BaSO_4$ (200 mg) in methanol (80 mL) containing pure synthetic quinoline (200 μL). The mixture was stirred magnetically under an atmosphere of hydrogen until 2.2 L had been absorbed and the velocity of absorption had decreased noticably. After filtration through a pad of Celite, solvent was removed by rotary evaporation. The residual oily product was partitioned between ether (100 mL) and ice cold 10% HCl (60 mL). The organic phase was separated and then washed with 10% HCl (30 mL), water (30 mL), and saturated aqueous $NaHCO_3$ (30 mL). After the mixture was dried over Na_2SO_4, solvent was removed by rotary evaporation and the residual oil distilled under reduced pressure to afford (*Z*)-3-penten-1-ol (6.1 g, 75% yield) as a clear colorless oil: bp 138–140 °C (760 mm); ^1H NMR ($CDCl_3$) δ 1.64 (3 H, d, *J* = 5 Hz), 2.1–2.6 (3 H), 3.64 (2 H, t, *J* = 6.5 Hz), 5.1–6.0 (2 H).

The alcohol (5.1 g, 59 mmol) in ether (90 mL) was treated with PBr_3 (3.3 mL) and the mixture stirred overnight and then poured into ice-cold water (80 mL). The ether layer was separated, and the aqueous phase was extracted with ether (2 × 80 mL). The combined organic extract was washed with water, aqueous saturated $NaHCO_3$, and aqueous saturated NaCl and dried ($MgSO_4$). Distillation afforded (*Z*)-5-bromo-2-pentene (3.5 g, 40% yield) as a clear colorless oil: bp 130–134 °C (750 mm); ^1H NMR ($CDCl_3$) δ 1.65 (2 H, d, *J* = 6 Hz), 2.54 (2 H, q, *J* = 7 Hz), 3.40 (2 H, t, *J* = 7 Hz), 5.1–6.0 (2 H).

The bromide (3.4 g, 23 mmol) in ether (25 mL) was converted under an atmosphere of dry nitrogen to a Grignard reagent by reaction with magnesium turnings (0.65 g, 27 mmol). The Grignard reagent solution

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was cooled in an ice-water bath, and a solution of acrolein (1.3 g, 1.6 mL, 24 mmol) in ether (5 mL) was added dropwise with mechanical stirring. Then the reaction was stirred at 0 °C for 30 min, at 20 °C for 1 h, and at the boiling point under reflux for 1.5 h. After the mixture was cooled in an ice–water bath, 10% HCl in water (15 mL) was added. The organic layer was separated and the aqueous layer extracted with ether (2 × 25 mL). The combined organic extract was washed with water and then saturated aqueous NaCl and dried ($MgSO_4$). Solvent was removed by rotary evaporation and the product distilled under reduced pressure to afford crude hydroxydiene (1.0 g, 35% yield); bp 65–75 °C (12 mm). Further purification was achieved by preparative gas–liquid phase chromatography on a 4 ft × 0.25 in. column packed with 15% FFAP (free fatty acid phase) on 60/80 mesh Chromosorb W at 130 °C to afford pure (*Z*)-1,6-octadien-3-ol (**1y**): ^{1}H NMR ($CDCl_3$) δ 1.4–1.8 (6 H), 1.9–2.4 (2 H), 4.13 (H, q, *J* = 6.3 Hz), 4.9–6.2 (5 H).

Photobicyclization. In a representative procedure for photobicyclization, hydroxyheptadiene **1** (0.17 mol) in ether (200 mL) with $CuOTF)_2{\cdot}C_6H_6$ (0.4 g, 0.8 mmol, 0.9 mol % CuOTF) was irradiated for 21 h with an internal 450–W Hanovia mercury vapor lamp. The resulting solution was poured into a mixture of ice (100 g) and concentrated NH_4OH (100 mL). The aqueous phase was extracted with ether (100 mL), and the combined organic extracts were washed with saturated aqueous NaCl (100 mL) and dried (Na_2SO_4). Solvent was removed by rotary evaporation and the product isolated by distillation under reduced pressure. Yields and ratios of C-2 epimers are listed in Table III. Hydroxybicycloalkanes **2a**, **2b**, and **2g** were characterized by comparison of their ^{1}H NMR spectra with data reported previously for the endo and exo epimeric isomers of each alcohol.[16,17]

3,3-Dimethylbicyclo[3.2.0]heptan-2-ols (2c): bp 85–89 °C (12 mm). The product was an epimeric mixture.

Anal. ($C_9H_{16}O$): C, H.

The epimers were separable by column chromatography on silica gel with ethyl acetate–hexane mixtures as eluting solvents. Analysis on a 0.25-mm silica gel thin layer with 20% ethyl acetate in hexane as developing solvent shows major (>90%) and minor (<10%) epimers with R_f's of 0.32 and 0.23, respectively. Analysis of the ^{1}H NMR spectrum of the photolysis product confirmed that the reaction was greater than 90% stereoselective in favor of the endo epimer. The major epimer, 3,3-dimethyl-*endo*-bicyclo[3.2.0]heptan-2-ol, showed the following: ^{1}H NMR ($CDCl_3$) δ 0.81 (3 H, s), 1.13 (3 H, s), 1.4–3.2 (9 H), 3.66 (H, d, *J* = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 16.3 (t, 22.5 (q, CH_3), 26.0 (t), 27.8 (q, CH_3), 36.0 (d), 42.8 (d), 45.5 (t), 45.8 (s, C-3), 80.9 (d, C-2). The minor epimer, 3,3-dimethyl-*exo*-bicyclo[3.2.0]heptan-2-ol, showed the following: ^{1}H NMR ($CDCl_3$) δ 0.77 (3 H, s), 1.08 (3 H, s), 1.2–2.9 (9 H), 3.80 (H, d, *J* = 4.6 Hz); ^{13}C NMR ($CDCl_3$) δ 20.7 (q, CH_3), 24.0 (t), 26.5 (q, CH_3), 27.1 (t), 34.6 (d), 45.6 (s, C-3), 45.8 (d), 46.7 (t), 88.7 (d, C-2).

4,4-Dimethylbicyclo[3.2.0]heptan-2-ols (2d): bp 91–94 °C (12 mm). The product was an epimeric mixture.

Anal. ($C_9H_{16}O$): C, H.

The epimers were separable by preparative gas–liquid phase chromatrography on a 4 ft × 0.25 in. column packed with 15% FFAP on 60/80 Chromosorb W at 120 °C. The major and minor epimers showed relative retention times of 1.00 and 1.19, respectively. The major epimer, 4.4-dimethyl-*exo*-bicyclo[3.2.0]heptan-2-ol, showed the following: ^{1}H NMR ($CDCl_3$) δ 0.97 (3 H, s), 1.10 (3 H, s), 1.1–3.0 (9 H), 4.11 (H, d, *J* = 5 Hz). The minor epimer, 4,4-dimethyl-*endo*-bicyclo[3.2.0]heptan-2-ol, showed the following: ^{1}H NMR ($CDCl_3$) δ 0.86 (3 H, s), 0.91 (3 H, s), 1.48 (H, s), 1.70 (H, s), 1.8–2.6 (6 H), 2.6–3.1 (H, m), 4.17 (H, q, *J* = 8 Hz).

1,3,3-Trimethylbicyclo[3.2.0]heptan-2-ols (2e): bp 95–98 °C (13 mm). The product was an epimeric mixture which showed the following: ^{1}H NMR ($CDCl_3$) δ 0.77 (1.8 H, s), 0.96 (1.2 H, s), 1.10 (1.2 H, s), 1.15 (3.6 H, s), 1.28 (1.2 H, s), 1.2–2.4 (8 H), 3.32 (0.4 H, s), 3.69 (0. 6 H, s).

Anal. ($C_{10}H_{18}O$): C, H.

1,5-Dimethyl-*endo*-bicyclo[3.2.0]heptan-2-ol (2f). The photobicyclization was only carried to 40% completion after 24 h. The bicyclic product **2f** was readily separable from staring hydroxydiene **1f** by preparative gas–liquid phase chromatography on a 10 ft × 0.25 in. column containing 10% Carbowax on 60/80 Chromosorb P at 150 °C. Relative retention times were 1.00 and 1.13 for **1f** and **2f**, respectively. The title bicyclic alcohol showed the following: ^{1}H NMR ($CDCl_3$) δ 1.00 (3 H, s), 1.05 (3 H, s), 1.2–2.1 (9 H), 3.67 (H, m).

Anal. ($C_9H_{16}O$): C, H.

***exo*-2-Methyl-*endo*-bicyclo[3.2.0]heptan-2-ol (2h)**: bp 75 °C (12 mm); ^{1}H NMR ($CDCl_3$) δ 1.17 (3 H, s), 1.3–2.9 (11 H).

Anal. ($C_8H_{14}O$): C, H.

6-Methylbicyclo[3.2.0]heptan-2-ols (2y). Analysis of the photobicyclization product by gas–liquid phase chromatography on a 4 ft × 0.25 in. column packed with 15% FFAP on 60/80 Chromosorb W at 130 °C revealed four products in a ratio of 4:50:3:43 with relative retention times of 1.00, 1.11, 1.30, and 1.46 respectively. Two epimeric mixtures were obtained by preparative gas–liquid phase chromatographic separation. Fraction A containing the epimers of relative retention times 1.00 and 1.11 showed the following: ^{1}H NMR ($CDCl_3$) δ 0.88 (3 H, d, *J* = 6 Hz), 1.3–3.0 (10 H), 3.9–4.4 (H). The presence of a minor epimer was evident from a CH_3 doublet centered at δ 0.85. Fraction B containing the epimers of relative retention times 1.30 and 1.46 showed the following: ^{1}H NMR ($CDCl_3$) δ 1.13 (3 H, d, *J* = 6 Hz), 1.3–2.4 (9 H), 2.4–2.9 (H), 4.0–4.4 (H). These epimeric mixtures were characterized further by oxidative conversion into the corresponding ketones (vide infra).

Bicyclo[3.2.0]heptan-2-ones (3). In a representative procedure for oxidation, 2-hydroxybicyclo[3.2.0]heptane **2** (0.25 mol) and acetone (200 mL) in a 500-mL flask was cooled with an ice–water bath while 2.7 M Jones reagent[37] (100 mL) was added portionwise over 15 min with vigorous mechanical stirring. The ice–water bath was removed, and the reaction mixture was stirred at 5–20 °C for 2 h. Then saturated aqueous NaCl (400 mL) was added, and the product was extracted into ehter (3 × 500 mL). The combined extracts were washed with saturated aqueous NaCl (400 mL) and saturated aqueous $NaHCO_3$ (200 mL). Solvents were removed by rotory evaporation, and the product was separated from some water which was washed with ether (50 mL). The product and ether washings were combined and dried over Na_2SO_4. Solvent was removed by rotary evaporation and the product distilled under reduced pressure. Yields for **3a–e** are listed in Table IV. Bicyclo[3.2.0]heptan-2-ones **3a**, **3b**, and **3g** were characterized by comparison of their ^{1}H NMR spectra with reported data.[16,17]

3,3-Dimethylbicyclo[3.2.0]heptan-2-one (3c): bp 72–75 °C (12 mm); ^{1}H NMR (CCl_4) δ 0.92 (3 H, s), 1.12 (3 H, s), 1.4–3.8 (8 H); ^{13}C NMR ($CDCl_3$) δ 22.7 (t), 24.1, 25.6 (d), 26.4, 31.0 (d), 43.9, 44.2, 48.4 (s, C-3), 173.6 (s, C-2).

Anal. ($C_9H_{14}O$): C, H.

4,4-Dimethylbicyclo[3.2.0]heptan-2-one (3d): bp 77–78 °C (13 mm); ^{1}H NMR (CCl_4) δ 0.90 (3 H, s), 1.03 (3 H, s), 1.3–2.43 (6 H), 2.43–2.8 (2 H).

Anal. ($C_9H_{14}O$): C, H.

1,3,3-Trimethylbicyclo[3.2.0]heptan-2-one (3e): bp 82–84 °C (13 mm); ^{1}H NMR (CCl_4) δ 0.93 (3 H, s), 1.16 (3 H, s), 1.25 (3 H, s), 0.9–2.5 (7 H).

Anal. ($C_{10}H_{16}O$): C, H.

***exo*-6-Methylbicyclo[3.2.0]heptan-2-one (*exo*-3y).** Oxidation of the epimeric 6-methylbicyclo[3.2.0]heptan-2-ols contained in fraction A of **2y** produced the title epimer of **3y** exclusively. The absence of any *endo*-**3y** in the product was demonstrated by gas–liquid phase chromatography on a 4 ft × 0.25 in. column packed with 15% FFAP on 60/80 mesh Chromosorb W at 110 °C. The exo and endo epimers were well resolved on this column with relative retention times 1.00 and 1.49, respectively. The exo epimer showed the following: ^{1}H NMR ($CDCl_3$) δ 1.15 (3 H, d, *J* = 6 Hz), 1.7–2.3 (5 H), 2.3–2.8 (4 H); ^{13}C NMR ($CDCl_3$) δ 223.3 (s, C-2), 43.8 (d), 41.6 (d), 36.9 (t), 33.5 (d), 30.3 (t), 26.9 (t), 21.7 (q, C-6). These spectra were in complete agreement with data reported previously[25] for *exo*-**37** except that off-resonance experiments which we were able to perform now showed that the resonances reported at δ 33.68 and 30.34 were coupled with one and with two protons, respectively.

***endo*-6-Methylbicyclo[3.2.0]heptan-2-one (*endo*-3y).** Oxidation of the epimeric 6-methylbicyclo[3.2.0]heptan-2-ols contained in fraction B of **2y** produced the title epimer of **3y** exclusively as shown by gas–liquid phase chromatography (vide supra). The endo epimer showed the following: ^{1}H NMR ($CDCl_3$) δ 1.03 (3 H, d, *J* = 6 Hz), 1.4–1.8 (H), 1.8–2.2 (2 H), 2.2–3.2 (6 H); ^{13}C NMR ($CDCl_3$) δ 221.7 (s, C-2), 42.3 (d), 38.2 (t), 37.3 (d), 31.6 (t), 29.3 (d), 20.9 (t), 16.6 (q, C-6). These spectra are in complete agreement with data reported previously[25] for *endo*-**3y**.

Thermolysis of Bicyclo[3.2.0]heptan-2-ones. A stream of nitrogen (25–30 mL min^{-1}) was passed through a vertical quartz column (30 cm) packed with quartz chips and heated at 580–600 °C. The ketone **3** was added dropwise (0.1 mL min^{-1}) with a Sage syringe pump at the top of the column. The product was trapped in a receiver cooled to −78 °C and was distilled to give cyclopentenone **4**. Yields for **4a–e** are listed in Table IV. Cyclopentenones **4a–d** were characterized by comparison of their ^{1}H NMR spectra with those of authentic samples or reported data.

2,5,5-Trimethylcyclopent-2-en-1-one (4e): bp 113–115 °C (120 mm); ^{1}H NMR (CCl_4) δ 1.02 (6 H, s), 1.72 (3 H, m), 2.37 (2 H, m), 7.14 (H, m).

Anal. ($C_8H_{12}O$): C, H.

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Diethyl 4-Pentenylpropanedioate (9a). A 250-mL, three-necked, round-bottomed flask fitted with a reflux condenser topped with a head of dry nitrogen, a pressure equalizing addition funnel, and mechanical stirrer was charged with ethanol (90 mL) freshly distilled from NaOEt. Then sodium metal (4.16 g, 0.18 mmol) was added. After the initial vigorous reaction, the mixture was boiled under reflux until the sodium was completely dissolved. After the mixture was cooled, to ~50 °C, diethyl malonate (28.2 mL) was added slowly through the addition funnel. To the resulting solution was added gradually 5-bromo-1-pentene (26.8 g, 0.18 mol). The reaction commenced almost immediately, and considerable heat was generated. After the resulting mixture was refluxed for 3 h, the mixture was cooled, and the solvent was then removed by rotary evaporation. The residue was treated with 5% HCl in water (50 mL) and water (150 mL) and extracted with ether (2 × 50 mL). Removal of the solvent by rotary evaporation and distillation of the residue under reduced pressure afforded **9a** (35.4 g, 86% yield): bp 130–134 °C (15 mm); ^{1}H NMR ($CDCl_3$) δ 1.25 (6 H, 5, J = 7 Hz), 1.3–2.3 (6 H), 3.32 (H, t, J = 7 Hz), 4.18 (4 H, q, J = 7 Hz), 4.8–5.2 (2 H), 5.4–6.2 (H, m).

Anal. ($C_{12}H_{20}O_4$): C, H.

Diethyl 5-Hexenylpropanedionate (9b). This alkenyl malonate was prepared from 6-bromo-1-hexene in a procedure analogous with that described above for **9a**. The title compound was obtained in 82% yield: bp 143–145 °C (15 mm); ^{1}H NMR ($CDCl_3$) δ 1.25 (6 H, t, J = 7 Hz), 1.3–2.3 (8 H), 3.32 (H, t, J = 7 Hz), 4.18 (4 H, q, J = 7 Hz), 4.8–5.2 (2 H), 5.4–62 (H, m).

Anal. ($C_{13}H_{22}O_4$): C, H.

2-(Hydroxymethyl)-1,6-heptadiene (5a). A suspension of 57% NaH in mineral oil (2.7 g) was washed with pentane (2 × 50 mL) and then suspended with mechanical stirring under an atmosphere of dry nitrogen in 1,2-dimethoxyethane (70 mL) freshly distilled from sodium benzophenone ketyl. Diethyl 5-pentenylpropanedioate (**9a**) (10 g, 44 mmol, 10.3 mL) was added and the mixture stirred and maintained at reflux for 6 h. After the mixture was cooled, $LiAlH_4$ (4.4 g) was added cautiously with stirring. After the initial vigorous reaction subsided, the mixture was boiled under reflux and stirred for 3 h. After the mixture was cooled somewhat, ethyl formate (16 mL) was added cautiously and the resulting mixture stirred under reflux for 1 h; after the solution was cooled, water (4 mL), 15% NaOH (4 mL), and then water (12 mL) were cautiously added in succession with stirring. The resulting mixture was cooled, ether (100 mL) was added, and the resulting mixture was stirred for 1 h, at room temperature, and then filtered with suction on a Buchner funnel. The filter cake was thoroughly triturated with ether (2 × 50 mL), and the combined organic extracts were concentrated by rotary evaporation of solvents. Distillation of the residual oil under reduced pressure afforded the title compound (3.2 g, 58% yield), bp 85–952 (15 mm), which contained ~10% of 2-methyl-6-heptene-1-ol (**10a**). These products were separable by preparative 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 120 °C. The products **10a** and **5a** showed relative retention times of 1.0 and 1.3, respectively. The title compound showed the following: ^{1}H NMR ($CDCl_3$) δ 1.2–1.8 (2 H), 1.8–2.4 (4 H), 4.11 (2 H, s), 4.8–5.3 (4 H), 5.6–6.3 (H, m).

Anal. ($C_6H_{14}O$): C, H.

2-Methyl-6-hepten-1-ol (10a). The byproduct from the above reduction showed the following: ^{1}H NMR ($CDCl_3$) δ 0.92 (3 H, d, J = 6 Hz), 1.1–2.3 (8 H), 3.5 (2 H, m), 4.8–5.2 (2 H), 5.5–6.3 (H, m).

Anal. ($C_8H_{16}O$): C, H.

2-(Hydroxymethyl)-1,7-octadiene (5b). This hydroxydiene was prepared from diethyl 5-hexenylpropanedioate (**9b**) in a procedure analogous with that described above for **5a**. The reduction product obtained in 60% yield, bp 97–105 °C (15 mm), contained the title compound (86%) as well as 14% of 2-methyl-7-octen-1-ol (**10b**). These products were separable by preparative 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 150 °C. The products **10b** and **5b** showed relative retention times of 1.00 and 1.27, respectively. The title compound showed the following: ^{1}H NMR ($CDCl_3$) δ 1.2–1.7 (4 H), 1.8–2.3 (5 H), 4.10 (2 H, s), 4.8–5.3 (4 H), 5.4–6.3 (H).

Anal. ($C_9H_{16}O$): C, H.

2-Methyl-7-octen-1-ol (10b). The byproduct from the above reduction showed the following: ^{1}H NMR ($CDCl_3$) δ 0.91 (3 H, d, J = 6 Hz), 1.2–2.3 (10 H), 3.50 (H, d, J = 6 Hz), 4.8–5.3 (2 H, 5.4–6.3 (H, m).

Anal. ($C_9H_{18}O$): C, H.

3-(Acetoxymethyl)-1,2,7-octatriene (11). The synthetic strategy employed for preparing **11** was precedented.[38] A Grignard reagent was prepared from 5-bromo-2-pentene (14.9 g, 11.8 mL, 0.1 mol) in ether (100 mL) and magnesium turnings (3.6 g, 0.15 mol). The solution was transferred under dry nitrogen pressure through a polyethylene tube and a glass wool plug into a solution of 1,4-dibromo-2-butyne (20 g) in ether (50 mL). The reaction was vigorously exothermic and the ether was allowed to boil under reflux. After completion of the addition, the mixture was stirred magnetically at room temperature overnight. Then the mixture was hydrolyzed with a mixture of ice and ammonium chloride. The ether layer was separated and the aqueous layer extracted with ether (50 mL). The combined ether extracts were washed with water (3 × 10 mL) and dried (Na_2SO_4), and solvent was removed by rotary evaporation. The residue was distilled to afford 16 g (80% yield) of impure 3-(bromomethyl)-1,2,7-octatriene: bp 58–63 °C (0.03 mm). This product was purified by reaction with maleic anhydride (3 g), in acetone (30 mL) at 20 °C for 2 days. Then ether (60 mL) was added, and the solution was washed with 10% Na_2CO_3 (3 × 10 mL) and dried (Na_2SO_4), and solvent was removed by rotary evaporation to give purified allenic bromide (15.0 g, 74.6 mmol). This was dissolved in glacial acetic acid (68 mL) with freshly fused sodium acetate (13.5 g) and the mixture boiled under reflux for 2 h and then poured into water (300 mL). The resulting mixture was neutralized by addition of $NaHCO_3$ and then extracted with ether (3 × 100 mL). The ether extract was dried ($MgSO_4$) and solvent removed by rotary evaporation. Distillation of the residue under reduced pressure gave crude allenic acetate, bp 55–60 °C (0.02 mm) which was purified by preparative high performance liquid chromatography on a silica gel column with a Waters Model 500 prep HPLC using benzene as eluting solvent. Bulb to bulb distillation (~60 °C (0.02 mm)) afforded **11** (1.5 g): ^{1}H NMR ($CDCl_3$) δ 1.3–2.4 (6 H), 2.09 (H, s), 4.55 (H, t, J = 2.5 Hz), 4.68–4.94 (3 H), 5.09 (H, d, J = 5 Hz), 5.4–6.2 (H).

Anal. ($C_{11}H_{16}O_2$): C, H.

3-(Hydroxymethyl)-1,2,7-octatriene (5c). The acetate **11** (1.5 g, 8.3 mmol) in anhydrous methanol (90 mL) was treated with 1.4 M $Ba(OMe)_2$ (150 μL), and the mixture was allowed to stand at room temperature for 10 h. The base was removed by adding amberlyst 15 and then filtering through a pad of Celite. Removal of solvent by rotary evaporation gave crude alcohol (800 mg) which was chromatographed on a column of 60–200 mesh silica gel (68 g) using $CHCl_3$ as eluting solvent. After bulb to bulb distillation (~5/ °C (0.01 mm)), the title compound (620 mg, 55% yield) was obtained which showed the following: ^{1}H NMR ($CDCl_3$) δ 1.4–2.4 (7 H), 4.07 (2 H, t, J = 3 Hz), 4.8–5.2 (4 H), 5.4–6.1 (H).

Anal. ($C_9H_{14}O$): C, H.

Oct-7-en-2-yn-1-ol (12): Tetrahydrofuran (75 mL) containing triphenylmethane (~5 mg) was cooled to 0 °C and treated with a few drops of 1.6 N n-BuLi in hexane until a red color persists. Then α-ethoxyethyl propargyl ether (11.1 mL, 75 mmol) was added. Then n-BuLi in hexane (47 mL of 1.6 N, 75 mmol) was added dropwise at 0 °C until the yellow solution turned reddish orange. Then hexamethylphosphoramide (10 mL) was added followed by 5-bromo-1-pentene (11.2 g, 9.0 mL, 75 mmol). The resulting mixture was boiled under reflux overnight, cooled, poured into ice water (100 mL), and extracted with ether (3 × 100 mL). The combined extracts were washed with water (3 × 50 mL) and dried (Na_2SO_4), and solvent was removed by rotary evaporation. Distillation of the residue under reduced pressure afforded **1-(α-ethoxyethoxy)oct-7-en-2-yne** (12.4 g, 84% yield): bp 120–122 °C (15 mm); ^{1}H NMR ($CDCl_3$) δ 1.20 (3 H, t, J = 7 Hz), 1.34 (3 H, d, J = 5 Hz), 1.68 (2 H, m), 2.0–2.5 (4 H), 3.60 (2 H, m), 4.20 (2 H, t, J = 2 Hz), 4.6–5.2 (3 H), 5.4–6.1 (H, m).

Anal. ($C_{12}H_{20}O_2$): C, H.

The above α-ethoxyethyl ether (12 g, 61 mmol) was combined with methanol (90 mL), water (25 mL), and concentrated aqueous HCl (12 mL). The mixture was boiled under reflux for 3 h. After the mixture was cooled, methanol was removed by rotary evaporation below 30 °C. The product was extracted into ether (2 × 100 mL). The combined extracts were washed with water (20 mL) and saturated aqueous NaCl (20 mL) dired (Na_2SO_4), and concentrated by rotary evaporation of solvents. Distillation under reduced pressure afforded **12** (7.3 g, 97%): bp 100–101 °C (15 mm); ^{1}H NMR ($CDCl_3$) δ 1.2–2.5 (7 H), 4.25 (2 H, t, J = 2 Hz), 4.8–5.3 (2 H), 5.5–6.2 (H).

Anal. ($C_8H_{12}O$): C, H.

(*E*)-2,7-Octadien-1-ol (7*E*). A suspension of $LiAlH_4$ (4.5 g) in dry THF (200 mL) in a three-neck round-bottom flask fitted with mechanical stirrer and reflux condenser topped with a head of dry nitrogen was treated with the alkynol **12** dropwise with mechanical stirring (3.72 g, 3.94 mL, 30 mmol). The resulting mixture is boiled under reflux for 4 h. Then, with ice–water cooling, water (4.5 mL), 15% aqueous NaOH (4.5 mL), and water (13 mL) were cautiously added 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 × 30 mL), and the combined organic solutions were concentrated

(38) Lumbrosco-Bader, N.; Michel, E.; Troyanowsky, C. *Bull. Soc. Chim. Fr.* **1967**, 189.

by rotary evaporation of solvents. Distillation of the residual oil afforded hydroxydiene **7*E*** (3.3 g, 89%): bp 95–97 °C (14 mm); ^{1}H NMR ($CDCl_3$) δ 1.3–1.7 (2 H, m), 1.78 (H, s), 1.9–2.3 (4 H, m), 4.07 (2 H, m), 4.7–5.2 (2 H), 5.3–6.2 (3 H).

Anal. ($C_8H_{14}O$): C, H.

(*Z*)-2,7-Octadien-1-ol (7*Z*). Alkynol **12** (2.5 g) was added to a suspension of 5% Pd on $BaSO_4$ (70 mg) in methanol (25 mL) containing pure synthetic quinoline (70 mg, 2 drops). The mixture was stirred magnetically under an atmosphere of hydrogen until 450 mL was absorbed and the rate of absorption decreased noticably. Catalyst was removed by filtration through a pad of Celite. Solvent was removed by rotary evaporation. The residue was partitioned between ether (35 mL) and ice cold 10% HCl (20 mL). The organic phase was separated and then washed with 10% HCl (10 mL), water (10 mL), and saturated aqueous $NaHCO_3$. After the solution was dried (Na_2SO_4), solvent was removed by rotary evaporation and the residual oil distilled under reduced pressure to afford **7*Z*** (2.3 g, 92%): bp 96 °C (12 mm); ^{1}H NMR ($CDCl_3$) δ 1.3–1.8 (2 H, m), 1.87 (H, s), 1.9–2.3 (4 H), 4.16 (2 H, d, J = 5 Hz), 4.7–5.2 (2 H), 5.3–6.2 (3 H).

Anal. ($C_8H_{14}O$): C, H.

1-(Hydroxymethyl)bicyclo[3.2.0]heptane (6). Photobicyclization (vide supra) of 2-(hydroxymethyl)-1,6-heptadiene (**5a**) (2.7 g, 21 mmol) containing ~10% of 2-methyl-6-hepten-1-ol (**10a**), in ether (200 mL) in the presence of $(CuOTf)_2{\cdot}C_6H_6$ (0.23 g) for 16 h, provided **6** (2.6 g, 96%), bp 99–104 °C (15 mm), which contained ~10% of **10a**. These compounds were readily separable 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 120 °C. The alcohols **10a** and **6** showed relative retention times of 1.0 and 1.5 respectively. The title compound **6** showed the following: ^{1}H NMR ($CDCl_3$) δ 1.2–1.7 (6 H), 1.7–2.2 (5 H), 2.2–2.7 (H), 3.59 (2 H, s); ^{13}C NMR ($CDCl_3$) δ 69.3 (t, CH_2OH), 50.4 (s), 39.1 (d), 35.9 (t), 33.5 (t), 26.0 (t), 25.6 (t), 21.1 (t).

Anal. ($C_8H_{14}O$): C, H.

6-(Hydroxymethyl)bicyclo[3.2.0]heptane (8) from 7*E*. Photobicyclization (vide supra) of (*E*)-2,7-octadien-1-ol (**7*E***) (3.0 g, 24 mmol) in ether (200 mL) in the presence of $(CuOTf)_2{\cdot}C_6H_6$ (0.22 g) for 16 h provided **8** (2.8 g, 93%), bp 99–102 °C (15 mm), which was clearly a (3:1) mixture of C-6 epimers which were only partially separable by gas–liquid phase chromatography at 175 °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 **19x** and **19n** were 1.00 and 1.16, respectively.

Anal. ($C_8H_{14}O$): C, H.

The epimers **19x** and **19n** were separated indirectly by conversion to the acetates **20** which were more readily separated followed by regeneration of the pure epimeric alcohols from the corresponding acetates.

6-(Acetoxymethyl)bicyclo[3.2.0]heptane (20). Epimeric mixture of **19x** and **19n** (220 mg, 1.75 mmol) in dry CH_2Cl_2 (3 mL) with dry triethylamine (0.5 mL), *p*-(*N*,*N*-dimethylamino)pyridine (50 mg), and acetic anhydride (1.0 mL) was kept at 20 °C for 1 day. The reaction mixture was poured into a mixture of crushed ice (2 g), water (2 mL), and concentrated HCl (3 mL) and extracted with ether (3 × 10 mL). The extract was washed with aqueous 10% HCl (3 × 10 mL) and saturated aqueous NaCl (10 mL) and dried ($MgSO_4$). Removal of solvent by rotary evaporation followed by high vacuum (0.03 mm) afforded an epimeric mixture of acetates **20** (250 mg, 79% yield) which were separated by preparative gas–liquid phase chromatography at 110 °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 **20x** and **20n** were 1.00 and 1.16, respectively. ***exo*-6-(Acetoxymethyl)bicyclo[3.2.0]heptane (20x)** showed the following: ^{1}H NMR ($CDCl_3$) δ 1.4–1.9 (8 H), 2.03 (3 H, s), 2.1–2.9 (3 H), 4.06 (2 H, d, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 171.4 (s, C=O), 68.8 (t, CH_2OAc), 41.1 (d), 36.0 (d), 34.5 (d), 33.2 (t), 32.9 (t), 27.1 (t), 24.9 (t), 21.0 (q, CH_3). ***endo*-6-(Acetoxymethyl)bicyclo[3.2.0]heptane (20n)** showed the following: ^{1}H NMR ($CDCl_3$) δ 1.0–2.0 (7 H), 2.01 (3 H, s), 2.1–3.0 (4 H), 3.97 (2 H, d, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 171.3 (s, C=O), 64.8 (t, CH_2OAc), 39.0 (d), 35.5 (d), 32.7 (t), 31.0 (d), 27.3 (t), 27.2 (t), 26.4 (t), 21.0 (q, CH_3).

Regeneration of Alcohols 19 from Acetates 20. A solution containing acetate **20x** (400 mg, 2.22 mmol) in dry MeOH (50 mL) was treated with a solution of $Ba(OMe)_2$ in MeOH (100 μL of 1 M). After the mixture was left standing at 20 °C for 20 h, base was neutralized by stirring with Amberlyst 15. The ion-exchange resin was removed by filtration through a pad of Celite. Solvent was removed by rotary evaporation followed by evacuation to 0.02 mm to afford ***exo*-6-(hydroxymethyl)bicyclo[3.2.0]heptane (19x)** (254 mg, 85% yield): ^{1}H NMR ($CDCl_3$) δ 1.2–2.9 (12 H), 3.63 (2 H, d, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 67.6 (t, CH_2OH), 40.9 (d), 39.4 (d), 34.6 (d), 33.2 (t), 33.0 (t), 26.9 (t), 25.0 (t).

Similar treatment of the minor epimeric acetate **20n** afforded ***endo*-6-(hydroxymethyl)bicyclo[3.2.0]heptane (19n)** in 96% yield: ^{1}H NMR ($CDCl_3$) δ 0.9–2.5 (8 H), 2.55 (H, s), 2.5–3.0 (3 H), 3.54 (2 H, d, J = 5.8 Hz); ^{13}C NMR ($CDCl_3$) δ 63.2 (t, CH_2OH), 38.9 (d), 35.4 (d), 34.5 (d), 33.3 (t), 32.8 (t), 27.2 (t), 26.6 (t).

***exo*-6-(Carbomethoxy)bicyclo[3.2.0]heptane (21x).** A solution of the exo alcohol **19x** (254 mg, 2.0 mmol) in acetone (3 mL) was cooled to 0–5 °C and treated with Jones reagent [37] (2.5 mL of 1.34 M), and the resulting mixture was stirred for 1 h and then at 20 °C for 3 h. The mixture was then poured into saturated aqueous NaCl (30 mL) and extracted with ether (3 × 30 mL). The extract was washed with saturated aqueous NaCl (3 × 15 mL), and then it was extracted with saturated aqueous $NaHCO_3$ (3 × 10 mL). The resulting aqueous extract was acidified with cold 6 N HCl and then extracted with ether (3 × 20 mL). The ether extracts were washed with saturated aqueous NaCl (20 mL), dried ($MgSO_4$), and concentrated by rotary evaporation of solvents to afford a carboxylic acid (237 mg, 85% yield). This was methylated with an excess of etheral diazomethane to afford **21x** which was identified as *exo*-6-(carbomethoxy)bicyclo[3.2.0]heptane which showed the following: ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.2–2.0 (7 H), 2.2–3.0 (4 H), 3.67 (3 H, s). This spectrum is consistent with that reported previously[35] for **21x** while that shown by **21n** (vide infra) is not.

***endo*-6-(Carbomethoxy)bicyclo[3.2.0]heptane (21n).** The minor epimeric endo alcohol **19n** was oxidized (76% yield) and methylated as for the exo epimer above. The endo ester **21n** showed the following: ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.2–2.4 (8 H), 2.5–3.1 (2 H), 3.28 (H, apparent q, J = 9 Hz), 3.67 (3 H, s).

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Registry No. 1a, 5903-39-9; **1b**, 53268-46-5; **1c**, 58144-16-4; **1d**, 71221-65-3; **1e**, 71221-66-4; **1f**, 29765-76-2; **1g**, 79972-54-6; **1h**, 34780-69-3; **1y**, 79972-55-7; *exo*-**2a**, 41398-40-7; *endo*-**2a**, 41398-39-4; *exo*-**2b**, 50560-17-3; *endo*-**2b**, 50560-18-4; *exo*-**2c**, 80008-89-5; *endo*-**2c**, 80008-90-8; *exo*-**2d**, 80008-91-9; *endo*-**2d**, 80008-92-0; *exo*-**2e**, 80008-93-1; *endo*-**2e**, 80008-94-2; **2f**, 80008-95-3; *exo*-**2g**, 50459-36-4; *endo*-**2g**, 50459-37-5; **2h**, 79972-56-8; *endo,exo*-**2y**, 79972-57-9; *exo,exo*-**2y**, 80008-96-4; *endo,endo*-**2y**, 80008-97-5; *exo,endo*-**2y**, 80008-98-6; **3a**, 29268-42-6; **3b**, 50459-43-3; **3c**, 71221-70-0; **3d**, 71221-71-1; **3e**, 71221-72-2; *exo*-**3y**, 74892-18-5; *endo*-**3y**, 74892-16-3; **4a**, 930-30-3; **4b**, 1120-73-6; **4c**, 17197-84-1; **4d**, 22748-16-9; **4e**, 71221-73-3; **5a**, 79972-58-0; **5b**, 79972-59-1; **5c**, 79972-60-4; **6**, 79972-61-5; (*E*)-**7**, 62179-18-4; (*Z*)-**7**, 79972-62-6; **8**, 79972-63-7; **9a**, 1906-96-3; **9b**, 69298-59-5; **10a**, 67133-86-2; **10b**, 79972-64-8; **11**, 79972-65-9; **12**, 79972-66-0; **19x**, 80008-99-7; **19n**, 80009-00-3; **20x**, 79972-67-1; **20n**, 80009-01-4; **21x**, 79972-68-2; **21n**, 80009-02-5; 4-pentenal, 2100-17-6; 2,2-dimethyl-4-pentenal, 5497-67-6; bromoethene, 593-60-2; 2-bromo-1-propene, 557-93-7; 3-(α-ethoxyethoxy)-1-lithiopropyne, 79761-43-6; 5-bromo-1-pentene, 1119-51-3; 3-pentyn-1-ol, 10229-10-4; (*Z*)-3-penten-1-ol, 764-38-5; (*Z*)-5-bromo-2-pentene, 50273-84-2; acrolein, 107-02-8; 6-bromo-1-hexene, 2695-47-8; 3-(bromomethyl)-1,2,7-octatriene, 79972-69-3; α-ethoxyethyl propargyl ether, 18669-04-0; 1-(α-ethoxyethoxy)oct-7-en-2-yne, 79972-70-6; 3,3-dimethyl-4-pentenal, 919-93-7; 4-methyl-4-pentenal, 3973-43-1; CuOTf, 42152-44-3.