A Copper(I)-Catalyzed Photobicyclization Route to *exo*-1,2-Polymethylene- and 7-Hydroxynorbornanes. Nonclassical 2-Bicyclo[3.2.0]heptyl and 7-Norbornyl Carbenium Ion Intermediates[1]

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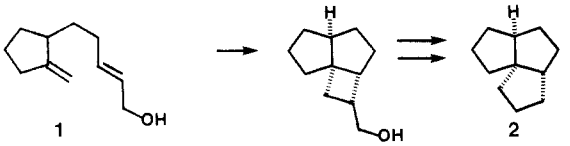
A synthesis of 7-hydroxynorbornanes from 3-hydroxy-1,6-heptadienes is achieved by copper(I) trifluoromethanesulfonate catalyzed $2\pi + 2\pi$ photobicyclization and solvolytic rearrangement of intermediate cyclobutylcarbinyl alcohols. The rearrangements are remarkably stereoselective and stereospecific. *exo*-1,2-Polymethylene-7-hydroxynorbornanes are obtained stereoselectively from both *cis*- and *trans*-2-allyl-1-vinylcycloalkanols owing to rapid cis–trans epimerization at the 3-position of intermediate 2,3-polymethylenebicyclo[3.2.0]hept-2-yl carbenium ions. The importance of bridged (nonclassical) carbenium ion intermediates in the 2-bicyclo[3.2.0]heptyl to 7-norbornyl rearrangements is poignantly evidenced by stereospecific inversion at the migration origin which delivers 1,2,2-trimethylnorbornan-*syn*-7-ol in the face of a severe countervailing steric impediment.

We previously demonstrated that copper(I)-catalyzed[2] $2\pi + 2\pi$ photobicyclization of 1,6-heptadienes readily accommodates substrates with allylic hydroxyl substituents.[3] This discovery is of special interest since a hydroxyl substituent might facilitate useful transformations of the photoproducts via cyclobutylcarbinyl to cyclopentyl ring-expanding rearrangements.[4] Our construction of tricyclo[6.3.0.0^{1,5}]undecane (**2**) from **1** provided the first example of the utility of this approach for the synthesis of multicyclic carbon networks.[3b] We now report successful



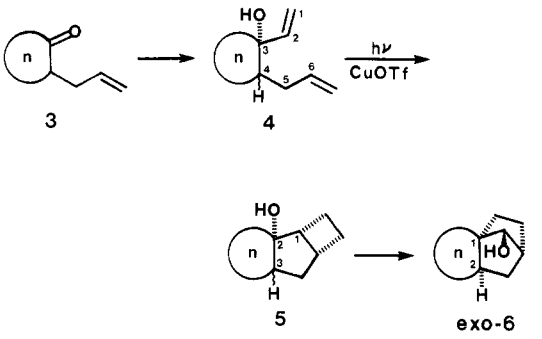
1 2

application of this concept to a versatile and efficient method for construction of 7-hydroxynorbornanes. Owing to rapid cis–trans epimerization at the 3-position of intermediate 2,3-polymethylenebicyclo[3.2.0]hept-2-yl carbenium ions, *exo*-1,2-polymethylene-7-hydroxynorbornanes *exo*-**6** were obtained stereoselectively from either *cis*- or *trans*-3,4-polymethylene-3-hydroxy-1,6-heptadienes **4** (Scheme I).

Results and Discussion

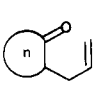
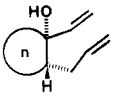
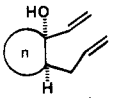
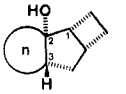
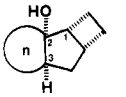
(A) Synthesis of Bicyclo[3.2.0]heptan-2-ols. Addition of vinylmagnesium bromide to 2-allylcycloalkanols **3**,[5] n = 5–8, occurred stereoselectively. A cis relationship between the hydroxyl and allyl substituents is presumed for the major isomers by analogy with the corresponding reactions of 2-methylcyclopentanone[6] and 2-methylcyclohexanone[7] with vinylmagnesium bromide. The outstandingly high stereoselectivity, a 98:2 preference for generating *cis*-**4c** vs. *trans*-**4c**, in the addition of vinylmagnesium bromide to 2-allylcycloheptanone (**3c**) is noteworthy (Table I).

Scheme I



3 4 5 exo-6

Table I. Synthesis of 2,3-Polymethylenebicyclo[3.2.0]heptan-2-ols from 2-Allylcyclohexanones[8]

allyl ketone	2-allyl-1-vinylcycloalkanol yield, %		bicyclo[3.2.0]heptanol yield, %	
				
3	cis-4	trans-4	endo-5	exo-5
a, n = 5	77	7.7	70	75
b, n = 6	84	6.3	51	84
c, n = 7	88	1.8	73	
d, n = 8	82	9.1	74	

A single stereoisomeric 2,3-polymethylenebicyclo[3.2.0]heptan-2-ol **5** was produced from each stereoisomeric hydroxy diene **4** upon ultraviolet irradiation in the presence of copper(I) trifluoromethanesulfonate[9] as catalyst. Ample precedent[3a] leads to the expectation of a cis relationship between the hydroxyl substituent and the cyclobutane ring in the products **5**. The relatively low yield of the trans-fused cyclohexanol *endo*-**5b** from *exo*-**4b** resulted from the generation of significant quantities of an unsaturated dehydration product which was isolated in 28% yield. A structure **7** is assigned to this alkene since vinyl

(1) Copper(I) Catalysis of Olefin Photoreactions. 14. For paper 13 in this series, see: Avasthi, K., Raychaudhury, S. R.; Salomon, R. G. *J. Org. Chem.* **1984**, *49*, 4322.
(2) For a recent review of homogeneous metal catalysis in organic photochemistry, see: Salomon, R. G. *Tetrahedron* **1983**, *39*, 485.
(3) (a) Salomon, R. G.; Coughlin, D. J.; Ghosh, S.; Zagorski, M. G. *J. Am. Chem. Soc.* **1982**, *104*, 998. (b) Salomon, R. G.; Ghosh, S.; Zagorski, M. G.; Reitz, M. *J. Org. Chem.* **1982**, *47*, 829.
(4) (a) Winstein, S.; Gadient, F.; Stafford, E. T.; Klinedinst, P. E., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 5895. (b) Funke, B.; Winstein, S. *Tetrahedron Lett.* **1971**, 1477. (c) Kirmse, W.; Siegfried, R.; Streu, J. *J. Am. Chem. Soc.* **1984**, *106*, 2465.
(5) (a) Howard, W. L.; Lorette, N. B. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. 5, p 25. (b) Araujo, H.; Mahajan, J. R. *Synthesis* **1978**, 228.
(6) Battioni, J. P.; Capmau, M. L.; Chodkiewicz, W. *Bull. Soc. Chim. Fr.* **1969**, 976.
(7) Marcou, A.; Normant, H. *Bull. Soc. Chim. Fr.* **1965**, 3491.
(8) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889.
(9) Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, 68.

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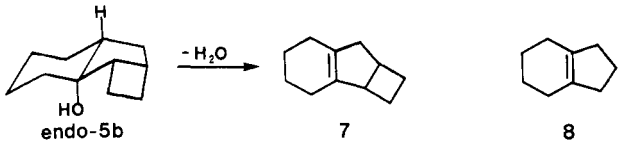
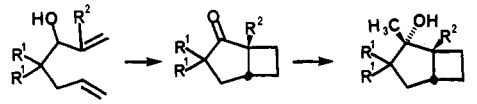
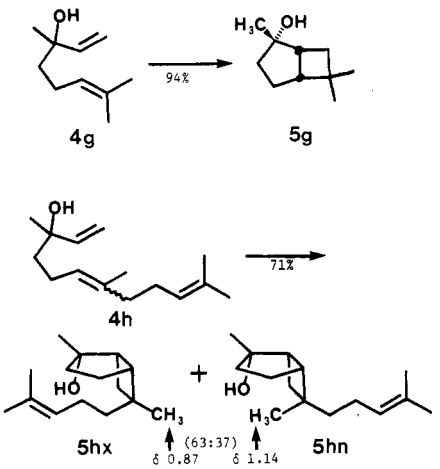
hydrogen resonances are not present in the ^1H NMR spectrum and the vinyl carbon NMR resonances at δ 134 and 137 are similar to the δ 134 resonance found for the vinyl carbons of 8.[9]



Bicyclo[3.2.0]heptan-2-ones **9e** and **9f** are readily available from 3-hydroxy-1,6-heptadienes **4e** and **4f** by ultraviolet irradiation in the presence of CuOTf followed by oxidation with CrO_3 in aqueous H_2SO_4.[10] These ke-



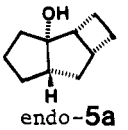
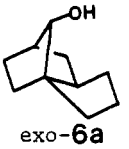
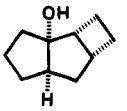
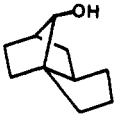
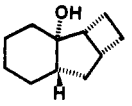
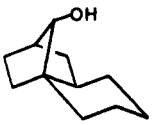
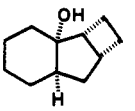
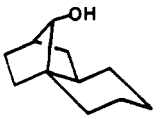
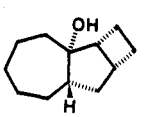
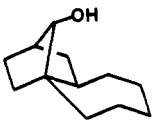
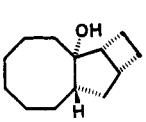
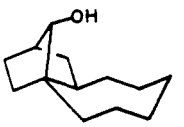
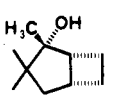
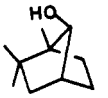
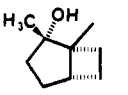
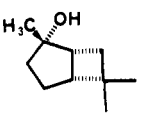
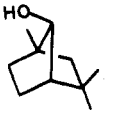
tones react stereoselectively with methyllithium to provide *endo*-2-hydroxybicyclo[3.2.0]heptanes **5e** and **5f**, respectively. Linalool (**4g**) affords **5g** while nerolidol (**4h**) affords a 63:37 mixture of **5hx** and **5hn**, respectively, upon ultraviolet irradiation in the presence of CuOTf. The endo



configuration of the methyl group at position 6 in **5hn** is evidenced by a downfield shift of its ^1H NMR resonance owing to the proximity of the endo hydroxyl substituent at position 2. Thus, the resonance for the hydrogens of this methyl group occurs at δ 1.14 compared with δ 0.87 for the corresponding methyl group in **5hx**.

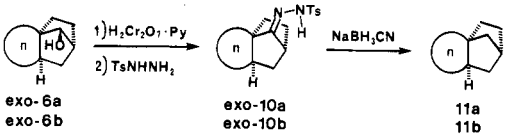
(B) Synthesis of 7-Hydroxynorbornanes. 1,2-Polymethylenenorbornanes. Solvolysis of the cyclobutylcarbinyl alcohols **5a–d** in boiling 90% trifluoroacetic acid followed by saponification of the resulting trifluoroacetates afforded rearranged alcohols **6** in good yields (Table II). The synthetic utility of this sequence was enhance by the discovery that solvolytic rearrangement of either the 2-exo or 2-endo epimer of **5a** affords *the same isomer* of **6a** with a 98:2 stereoselectivity. Similarly, stereoselective rearrangement of either the 2-exo or 2-endo epimer of **5b** favors the same isomer of **6b** by 97:3. In both cases the favored 1,2-polymethylenenorbornan-7-ol **6** was shown to be the 2-exo epimer by conversion to the known hydrocarbons **11a**[11] and **11b**[12] as shown in eq 1, by reduction of the

Table II. Solvolytic Rearrangement of Bicycloheptanols

bicyclo[3.2.0]heptan-2-ol	7-hydroxynorbornane	yield, %
 endo-**5a**	 exo-**6a**	64 (<1.5)[a]
 exo-**5a**	 exo-**6a**	85 (<1.5)[a]
 endo-**5b**	 exo-**6b**	77 (2.4)[a]
 exo-**5b**	 exo-**6b**	76 (2.1)[a]
 endo-**5c**	 exo-**6c**	73 (5.8)[a]
 endo-**5d**	 exo-**6d**	66 (17)[a]
 **5e**	 **6e**	43
 **5f**	 **6f**	47
 **5g**	 **6g**	45

[a] Endo epimer.

derived tosylhydrazones *exo*-**10** with sodium cyanoborohydride.[13]

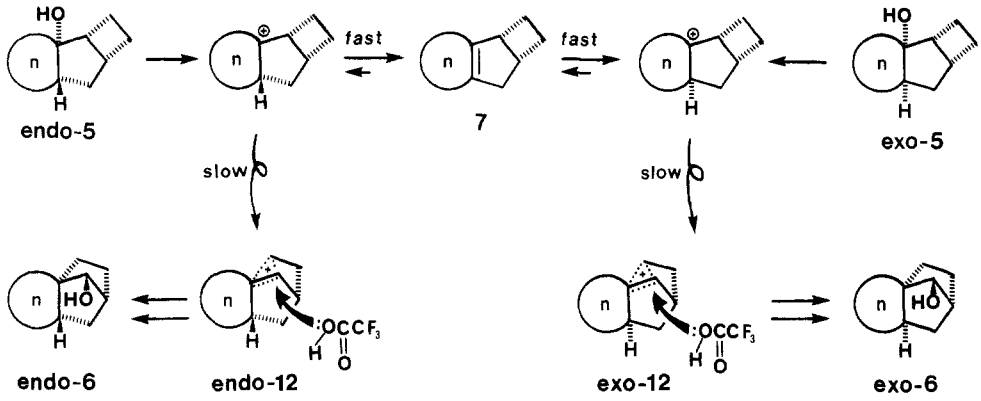


(1)

The same minor isomer of **6b** was produced by solvolytic rearrangement of either epimer of **5b**. The possibility was

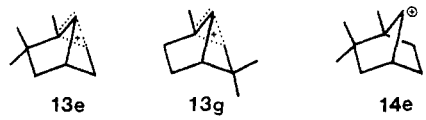
(10) Eisenbraun, E. J. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. 4, p 310.
(11) Jaggi, F. J.; Ganter, C. *Helv. Chim. Acta* **1980**, *63*, 866.
(12) Takaishi, N.; Inamoto, Y.; Tsuchihashi, K.; Yashima, K.; Aigami, K. *J. Org. Chem.* **1975**, *40*, 2929.
(13) Hutchins, R. O.; Milewski, C. A.; Maryanoff, B. E. *J. Am. Chem. Soc.* **1973**, *95*, 3662.

Scheme II



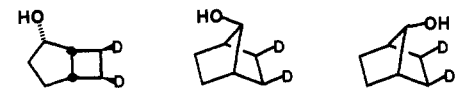
excluded that this minor product was simply the C-7 epimer of *exo*-**6b** since oxidation followed by reaction with tosylhydrazine did not afford *exo*-**10b**. Instead, the minor product is the C-2 epimer, *endo*-**6b**. Thus, the configuration at position 3 in *endo*-**5a** and *endo*-**5b** is stereoselectively epimerized during solvolytic rearrangement. The stereoselectivity decreases from less than 1.5% endo to 2.4% endo as the length of the polymethylene chain increases from three to four carbons in **5a** and **5b**, respectively. Epimerization also accompanies carbon skeletal rearrangement of *endo*-**5c** and *endo*-**5d**. By analogy with **5a** and **5b** the major solvolysis products are presumed to be the exo-2 isomers of **6c** and **6d**, with the proportion of endo-2 isomer formed increasing from 5.8% to 17% as the length of the polymethylene chain increases from five to six carbons. Thus, solvolytic cyclobutylcarbinyl to cyclopentyl rearrangements of the C-3 epimers of **5** is accompanied by equilibration of the C-3 stereocenters. A mechanism which can accommodate these observations is outlined in Scheme II. Support for this hypothesis was provided by solvation of the alkene **7b** with 90% trifluoroacetic acid which afforded a 97:3 mixture of *exo*-**6b** and *endo*-**6b**, respectively, after saponification of intermediate trifluoroacetates.

It is interesting that only a single C-7 epimer of *exo*- or *endo*-**6** is formed in these ring expansions. Similar results were obtained upon solvolytic rearrangement of **5e** and **5g** which each afforded a single epimeric alcohol (see Table II). Most remarkably, the 7-hydroxynorbornane **6e** produced from **5e** is clearly the sterically more congested epimer at position 7 with the hydroxyl substituent syn to the exo-2-methyl group. This is evident from the ^{1}H NMR spectrum of **6e** which shows methyl hydrogen resonance singlets at δ 0.95, 0.96, and 1.07. The low-field resonance results from a downfield shift of the exo-2-methyl group hydrogens owing to the proximity of the 7-hydroxyl. In contrast, the ^{1}H NMR spectrum of **6g**, produced from **5g**, shows methyl hydrogen resonances at δ 0.94, 0.98, and 0.98. The 7-hydroxy group is evidently anti to the exo-3-methyl group since no downfield shift is observed. Thus, **5e** and **5g** rearranged with inversion at the migration origin. This stereospecificity is readily explained by a preference for backside attack by the nucleophilic solvent on bridged carbenium ions **13e** and **13g**, respectively. For the un-



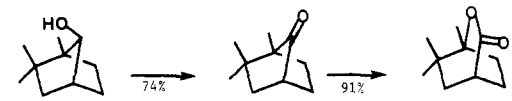
bridged carbenium ion **14e**, steric approach control of solvent capture would afford an epimeric mixture which, if anything, would favor generation of the anti epimer of **6e**. A stereoelectronic preference for backside attack by the nucleophilic solvent on bridged carbenium ions *endo*-**12** and *exo*-**12** (Scheme II) leads to assignment of the more sterically hindered configuration syn to the polymethylene bridges for the 7-hydroxyl substituent in *endo*-**6** and *exo*-**6**, respectively.

Very recently, Kirmse and Streu reported[14] compelling evidence for this same stereoelectronic effect and the involvement of bridged carbenium ion intermediates in solvolytic rearrangements of, inter alia, deuterium-labeled bicyclo[3.2.0]heptan-*endo*-2-ol **5i**. Thus acidolysis of **5i** produced *anti*-**6i**, and no *syn*-**6i** "within the limits of detection (1%)".[14] The **5i** to *anti*-**6i** rearrangement nicely



demonstrates a stereospecificity not expected for a classical 7-norbornyl carbenium ion intermediate. Instead, solvent capture of a bridged (nonclassical) 7-norbornyl carbenium ion intermediate with inversion at the migration origin is involved.[14] Our discovery of the stereospecific **5e** to **6e** rearrangement shows that this stereoelectronic effect operates even if a severe countervailing steric impediment is present. Thus, while the **5g** to **6g** rearrangement might be explicable in terms of steric approach control in solvent capture of a classical 7-norbornyl carbenium ion intermediate, the **5e** to **6e** rearrangement is diametrically opposed to such a mechanism.

Further synthetic applications of our photocyclization–solvolysis route to 7-hydroxynorbornanes are suggested by a regioselective conversion of **6e** into the lactone **16e** via Bayer–Villiger oxidation of the corresponding ketone **15e**.



It is important to note that our copper(I)-catalyzed photobicyclization route to *exo*-1,2-polymethylenenorbornanes is operationally simple. Since solvolytic rearrangements of C-3 epimers of **5a–d** are accompanied by equilibration of the C-3 stereocenters, separation of epimeric mixtures of the intermediates **4a–d** or **5a–d** is unnecessary. The efficiency of these syntheses supports our view that Cu(I)-catalyzed photocyclization of allylic alcohols in conjunction with solvolytic ring expansion will provide useful routes to a variety of multicyclic systems.[3b]

(14) Kirmse, W.; Streu, J. *J. Org. Chem.* **1985**, *50*, 4187.

Experimental Section

General. Irradiations were conducted under dry nitrogen in cylindrical Pyrex vessels with a quartz water-cooled double-walled immersion well. 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 A60-A or XL-200 spectrometer with tetramethylsilane as internal standard. Carbon magnetic resonance spectra were recorded with a Varian XL-200 spectrometer with tetramethylsilane as internal standard, and multiplicities refer to ^{13}C–^{1}H coupled spectra. Flash chromatography was performed with 150-mm long columns of Merck 230–400 mesh silica gel.[15] Column diameters are indicated in the text. Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI.

1-Vinyl-2-allylcyclohexanols (4b). To 0.5 M vinylmagnesium bromide in THF (200 mL) was added a solution of 2-allylcyclohexanone (10.53 g, 0.076 mol) in THF (25 mL) through a dropping funnel during 15 min. The reaction mixture was stirred 2 h at room temperature and then cooled in an ice bath, and excess vinylmagnesium bromide was quenched by careful addition of water. Most of the THF was removed by rotary evaporation, and the residue partitioned between water and ether (3 × 100 mL). The combined extracts were washed with brine (3 × 50 mL) and dried ($MgSO_4$), and the solvents were removed by rotary evaporation. Analysis of the residual yellow oil (23.66 g, quantitative) by HPLC (Partisil PXS 10/25, 8% ethyl acetate in *n*-hexane, 1 mL/min) showed two major products and less than 5% of unknown impurities. The two major alcohol products were formed in a 93:7 ratio and showed retention times of 7.5 and 11 min, respectively. The major product, **1-vinyl-*cis*-2-allylcyclohexanol (*cis*-4b)**, was isolated by flash column chromatography (10% ethyl acetate in hexane): ^{1}H NMR δ 1–1.92 (11 H), 2.0–2.36 (2 H, m), 4.96 (H, d, J = 10.4 Hz), 4.98 (H, d, J = 16.1 Hz), 5.09 (H, d, J = 10.7 Hz), 5.52 (H, d, J = 17.3 Hz), 5.5–5.9 (H, m), 5.85 (H, dd, J = 10.7, 17.3 Hz); ^{13}C NMR δ 21.2, 25.6, 26.1, 34.5, 38.8, 43.7, 74.4, 111.6, 225.4, 137.7, 145.8.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.60; H, 10.81.

The minor product, **1-vinyl-*trans*-2-allylcyclohexanol (*trans*-4b)**, was isolated by HPLC (Partisil M20 10/50, 7% ethyl acetate in hexane, 12 mL/min): ^{1}H NMR δ 1.1–1.8 (11 H), 2.30 (H, m), 4.97 (H, d, J = 10.6 Hz), 4.98 (H, d, J = 16.6 Hz), 5.17 (H, d, J = 11.1 Hz), 5.32 (H, d, J = 17.3 Hz), 5.64–5.94 (H, m), 6.20 (H, dd, J = 11.1, 17.3 Hz); ^{13}C NMR δ 23.3, 25.2, 28.4, 34.7, 40.4, 46.8, 74.9, 113.5, 115.5, 138.3, 140.0.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.58; H, 10.99.

1-Vinyl-2-allylcyclopentanols (4a). By a procedure analogous to that used for **4b** above, the alcohols **4a** were prepared from 2-allylcyclopentanone and vinylmagnesium bromide in 85% yield. The two isomeric alcohols obtained in a ratio of 91:9 showed HPLC retention times of 8.7 and 14.1 min, respectively (Partisil 1 ft column, 8% ethyl acetate in hexane). The major product, **1-vinyl-*cis*-2-allylcyclopentanol (*cis*-4a)**, showed the following: ^{1}H NMR δ 1.0–2.0 (9 H), 2.0–2.4 (H), 4.7–5.4 (4 H), 5.5–5.9 (H, m), 5.90 (H, dd, J = 10.8, 17.3 Hz); ^{13}C NMR δ 21.0, 29.1, 32.5, 40.4, 48.5, 82.3, 112.0, 114.5, 137.9, 143.6.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.31; H, 10.81.

The minor product, **1-vinyl-*trans*-2-allylcyclopentanol (*trans*-4a)**, was isolated by preparative HPLC (Partisil M 20 10/50, 7% ethyl acetate in hexane, 12 mL/min): ^{1}H NMR δ 1.0–1.3 (10 H), 4.78–5.38 (4 H, m), 5.58–5.90 (H, m), 5.98 (H, dd, J = 10.8, 17.3 Hz); ^{13}C NMR δ 20.6, 29.2, 35.5, 39.1, 50.1, 83.2, 112.3, 115.4, 137.8, 141.0.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.31; H, 10.81.

1-Vinyl-2-allylcycloheptanols (4c). Analysis of the crude product [95%, bp 50–54 °C (2 mm)] by HPLC (Partisil 1 ft, 10% ethyl acetate in hexane, 1 mL/min) showed unreacted ketone (4%) and two isomeric alcohol products in a 98:2 ratio which showed retention times of 8.8 and 10.6 min. the major product, **1-vinyl-*cis*-2-allylcycloheptanol (*cis*-4c)**, was isolated by flash chromatography (8% ethyl acetate in hexane): ^{1}H NMR δ 1.2–1.9 (13 H), 2.1–2.3 (H, ddd, J = 14.4, 5.3, 3.3 Hz), 4.9–5.2 (4 H, m), 5.7–5.8 (H, m), 5.93 (H, dd, J = 10.7, 17.2 Hz); ^{13}C NMR δ 21.4, 25.8, 28.5, 29.1, 35.3, 41.9, 46.9, 77.5, 110.7, 115.7, 138.3, 146.3.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.91; H, 11.18.

The minor product, **1-vinyl-*trans*-2-allylcycloheptanol (*trans*-4c)**, was isolated by preparative HPLC (Partisil M20 10/50, 7% ethyl acetate in hexane, 12 mL/min): ^{1}H NMR δ 1.06–2.0 (13 H), 2.20 (H, dm, J = 15.2 Hz), 4.9–5.1 (3 H, m), 5.19 (H, d, J = 17.2 Hz), 5.66–5.86 (H, m), 6.0 (H, dd, J = 10.8, 17.2 Hz); ^{13}C NMR δ 21.79, 28.19, 28.60, 30.10, 36.94, 43.10, 48.85, 78.38, 112.04, 115.98, 138.56, 142.70.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.10; H, 11.25.

1-Vinyl-2-allylcyclooctanols (4d). To a solution of vinylmagnesium bromide (16 mL of 1 M solution in THF) and 20 mL of THF was added a solution of 2-allylcyclooctanone (1.60 g, 9.64 mmol) in THF (5 mL) via a syringe during 10 min. The reaction mixture was stirred at room temperature for another 80 min. The reaction mixture was worked up as above for **4a**. Analysis of the crude reaction product by HPLC (Partisil PXS 10/25, 8% ethyl acetate in hexane, 0.7 mL/min) showed unreacted ketone (t_r 9.9 min) and two alcohol products in a 1:9 ratio (t_r = 14.2 and 15.3 min, respectively). The reaction mixture was purified by flash chromatography (60 mm, 8% ethyl acetate) to give 0.75 g (46.9%) of starting material and a mixture of the two alcohol products (0.90 g, 48.1% = 91% yield based on 53% conversion). The two isomeric alcohols were separated by preparative HPLC (Partisil M20 10/50, 6% ethyl acetate in hexane, 10 mL/min). The major product, **1-vinyl-*cis*-2-allylcyclooctanol (*cis*-4d)**, showed the following: ^{1}H NMR δ 1.2–2.0 (15 H), 2.20 (H, dm, J = 14.8 Hz), 4.99 (H, d, J = 10.4 Hz), 5.00 (H, d, J = 17.6 Hz), 5.10 (H, d, J = 10.8 Hz), 5.25 (H, d, J = 17.3 Hz), 5.6–5.8 (H, m), 6.03 (H, dd, J = 17.4, 10.8 Hz); ^{13}C NMR δ 22.7, 25.3, 26.57, 26.61, 29.8, 36.8, 38.0, 43.0, 77.9, 112.1, 115.8, 138.2, 145.1.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.41; H, 11.53.

The minor product, **1-vinyl-*trans*-2-allylcyclooctanol (*trans*-4d)**, showed the following: ^{1}H NMR δ 0.75–0.92 (H), 1.2–2.0 (14 H), 2.33 (H, dm, J = 13.6 Hz), 4.96 (H, d, J = 9.2 Hz), 4.98 (H, d, J = 17.3 Hz), 5.07 (H, d, J = 10.9 Hz), 5.20 (H, d, J = 17.5 Hz), 5.8–5.9 (H, m), 5.92 (H, dd, J = 17.3, 10.8 Hz); ^{13}C NMR δ 21.87, 25.88, 28.15, 28.38, 28.95, 37.25, 38.90, 42.10, 78.11, 112.37, 115.76, 138.84, 142.22.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.22; H, 11.51.

***exo*-2,*endo*-3-Tetramethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*endo*-5b).** A solution of 1-vinyl-*cis*-2-allylcyclohexanol (*cis*-**4b**) (4.22 g, 25.4 mmol) and $(CuOTf)_2 \cdot C_6H_6$ (0.55 g) in anhydrous ether (240 mL) was irradiated for 15 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 (10 mL). The aqueous phase was extracted with ether (2 × 50 mL), and the combined organic extracts were washed with brine (2 × 50 mL) and dried ($MgSO_4$). The solvents were removed by rotary evaporation to give a light yellowish brown oil, which was purified by flash chromatography (85-mm column, 8% ethyl acetate) to give 1.41 g of a less polar fraction and 2.16 g (51.2%) of *endo*-**5b** as a white solid, which showed: mp 69–70 °C: ^{1}H NMR δ 1.0–2.35 (17 H), 2.52–2.73 (H, m); ^{13}C NMR δ 17.3, 21.6, 25.5, 25.6, 29.3, 36.0, 37.0, 37.2, 48.3, 50.3, 77.6.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.59; H, 10.81.

The less polar fraction was repurified by flash chromatography (50 mm, hexane) to give 1.05 g (17.9%) of **2,3-tetramethylenebicyclo**[3.2.0]hept-2-ene (**7**); which showed the following: ^{1}H NMR δ 1.0–2.3 (13 H), 2.3–2.6 (H), 2.7–2.9 (H, m), 2.9–3.2 (H, br s); ^{13}C NMR δ 23.1, 23.3, 23.5, 25.9, 26.2, 27.7, 35.2, 44.2, 48.8, 134.2, 137.0.

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.13; H, 10.85.

***exo*-2,*endo*-3-Trimethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*endo*-5a).** A solution of 1-vinyl-*cis*-2-allylcyclopentanol (*cis*-**4a**)

(15) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(2.69 g, 17.68 mmol) and $(CuOTf)_2 \cdot C_6H_6$ (0.26 g) in anhydrous ether (240 mL) was irradiated for 14 h. Work up as for *endo*-**5b** above gave a yellowish brown product (2.55 g), which was purified by flash chromatography (70 mm, 10% ethyl acetate in hexane) to give 0.40 g of a less polar fraction and 1.88 g (69.9%) of *endo*-**5a**, which showed the following: ^1H NMR δ 1.1–2.4 (15 H), 3.0–3.2 (H, m); ^{13}C NMR δ 18.2, 21.7, 28.4, 29.1, 31.4, 33.3, 42.3, 45.0, 58.8, 91.1.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.97; H, 10.59.

***exo*-2,*endo*-3-Pentamethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*endo*-5c).** Irradiation of a solution of 1-vinyl-*cis*-2-allylcycloheptanol (*cis*-**4c**) (2.41 g, 13.38 mmol) and $(CuOTf)_2 \cdot C_6H_6$ (250 mg) in anhydrous ether (240 mL) for 16 h followed by workup as for *endo*-**5b** above gave a crude product (2.32 g), which upon purification by flash chromatography (70 mm, 8% ethyl acetate in hexane) provided *endo*-**5c** as a white solid (1.76 g, 73%): mp 68–69 °C; ^1H NMR δ 1.2–2.1 (18 H), 2.4–2.6 (2 H); ^{13}C NMR δ 17.8, 24.1, 25.5, 26.2, 26.6 (2 C), 36.6, 40.7, 41.7, 50.8, 51.5, 81.4.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.38; H, 11.44.

***exo*-2,*endo*-3-Hexamethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*endo*-5d).** A solution of 1-vinyl-*cis*-2-allylcyclooctanol (*cis*-**4d**) (1.71 g, 8.8 mmol) and $(CuOTf)_2 \cdot C_6H_6$ (0.22 g) in anhydrous ether (240 mL) was irradiated for 15 h. Work up as for *endo*-**5b** above gave 1.78 g of crude product, which was purified by flash chromatography (70 mm, 8% ethyl acetate in hexane) to give *endo*-**5d** (1.26 g, 73.7%), which showed the following: mp 41–42 °C; ^1H NMR δ 1.2–2.25 (20 H), 2.3–2.65 (2 H); ^{13}C NMR δ 17.5, 21.7, 25.3, 26.0, 26.3, 28.1, 29.9, 34.9, 38.4, 41.3, 46.9, 50.5, 80.1.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.10; H, 11.34.

***exo*-2,*endo*-3-Tetramethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*exo*-5b).** Irradiation of 1-vinyl-*trans*-2-allylcyclohexanol (*trans*-**4b**) (0.61 g, 3.67 mmol) and $(CuOTf)_2 \cdot C_6H_6$ (0.07 g) in anhydrous ether (240 mL) for 14 h followed by workup as for *endo*-**5b** above gave a light brown viscous liquid (0.68 g), which was purified by flash column chromatography (40 mm, 10% ethyl acetate in hexane) to give 0.51 g (83.6%) of *exo*-**5b** as a white crystalline solid: mp 66–67 °C; ^1H NMR δ 1.16–2.0 (14 H), 2.13–2.67 (4 H); ^{13}C NMR δ 17.5, 20.3, 21.9, 23.3, 24.9, 33.6, 33.9, 34.2, 40.5, 47.8, 78.2.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.45; H, 10.92. Found: C, 79.46; H, 10.92.

***exo*-2,*exo*-3-Trimethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*exo*-5a).** Irradiation of 1-vinyl-*trans*-2-allylcyclopentanol (*trans*-**4a**) (0.37 g, 2.44 mmol) and $(CuOTf)_2 \cdot C_6H_6$ (0.05 g) in anhydrous ether (240 mL) for 13 h followed by workup as for *endo*-**5b** above gave a light brown liquid (0.46 g), which was purified by flash column chromatography (40 mm, 10% ethyl acetate in hexane) to give 0.28 g (75%) *exo*-**5a** as a colorless liquid which showed the following: ^1H NMR δ 1.18–1.44 (H, m), 1.44–1.72 (6 H), 1.72–2.08 (5 H), 2.10–2.35 (H, m), 2.43–2.80 (3 H); ^{13}C NMR δ 18.9, 23.0, 24.6, 28.6, 37.1, 38.6, 38.7, 45.4, 49.1, 92.3.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.75; H, 10.55.

2,3,3-Trimethylbicyclo[3.2.0]heptan-*endo*-2-ol (5e). To a solution of methyllithium (46.5 mL of 1.4 M in ether, 0.065 mol) in dry THF (200 mL) was added 3,3-dimethylbicyclo[3.2.0]heptan-2-one[16] (7.60 g, 0.55 mol) dropwise at 0 °C under dry nitrogen. The reaction mixture was stirred for 15 min at 0 °C and 2 h at room temperature. The reaction mixture was again cooled to 0 °C and excess methyllithium was quenched by careful addition of water. The organic phase was separated and the aqueous phase extracted with ether (3 × 50 mL). The combined organic extracts were washed with brine and then dried ($MgSO_4$). The solvent was removed by rotary evaporation. Distillation of the residue gave **5e** (7.69 g, 90.7%): bp 86–89 °C (12 mm); ^1H NMR (60 MHz) δ 0.73 (3 H, s), 1.02 (3 H, s), 1.08 (3 H, s), 1.40 (H, s), 1.4–2.4 (6 H), 2.4–2.8 (2 H); ^{13}C NMR δ 16.9, 21.2, 22.1, 25.2, 27.3, 34.3, 47.3, 48.0, 48.1, 81.1.

(16) Salomon, R. G.; Ghosh, S. *Org. Synth.* **1984**, *62*, 125.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.62; H, 11.76.

1,2-Dimethylbicyclo[3.2.0]heptan-*endo*-2-ol (5f). This compound was prepared by the addition of 1-methylbicyclo-[3.2.0]heptan-2-one to a solution of methyllithium in ether at 0 °C. Alcohol **5f**, obtained in 90.8% yield, showed the following: mp 58–59 °C; ^1H NMR δ 1.11 (3 H, s), 1.13 (3 H, s), 1.3–1.55 (4 H), 1.59–1.83 (2 H, m), 2.0–2.42 (4 H); ^{13}C NMR δ 20.1, 21.1, 23.4, 26.3, 29.4, 39.9, 41.9, 48.5, 80.4.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.09; H, 11.43.

2,6,6-Trimethylbicyclo[3.2.0]heptan-*endo*-2-ol (5g). A solution of linalool (6.86 g, 0.044 mol) and copper(I) trifluoromethanesulfonate–benzene complex (0.49 g) in anhydrous ether (420 mL) was irradiated 14 h with a 450-W Hanovia lamp in a quartz immersion well. After completion of the irradiation, the reaction mixture was poured into a mixture of crushed ice (100 g) and 30% NH_4OH (10 mL). The deep blue aqueous phase was separated and extracted with ether (2 × 50 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. Removal of the solvents by rotary evaporation gave **5g** as a light yellow solid (6.45 g, 94%)), which was then distilled under reduced pressure: bp 94–96 °C (16 mm); mp 60–62 °C; ^1H NMR δ 0.88 (3 H, s), 1.14 (3 H, s), 1.18 (3 H, s), 1.5–1.7 (5 H), 1.8–2.0 (H, m), 2.11 (H, s), 2.14 (H, t, J = 7.6 Hz), 2.33 (H, q, J = 7.4 Hz); ^{13}C NMR δ 23.5, 24.4, 27.3, 31.9, 32.2, 33.4, 38.7, 41.8, 46.1, 78.9. An analytical sample was obtained by flash chromatography (10% ethyl acetate in hexane).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.65; H, 11.64.

Irradiation of Nerolidol. A solution of nerolidol (7.08 g, 32 mmol) and copper(I) trifluoromethanesulfonate–benzene complex (0.31 g) was irradiated 16 h as described for linalool. The crude product (6.81 g, 96%) showed no terminal vinyl protons in the ^1H NMR, indicating complete consumption of starting material. Purification of the crude product by HPLC (Waters 500A, silica gel, 12.5% ethyl acetate in hexane) gave 5.03 g (71%) of cyclized product. ^1H NMR analysis of the product indicated a 3:2 mixture of two isomers. The major product was only slightly more polar than the minor isomer on an analytical HPLC column. Pure samples of each isomer were obtained by HPLC (Partisil M20 10/50, 7% ethyl acetate in hexane). The major isomer (**5hx**) showed the following: mp 56–58 °C; ^1H NMR δ 0.86 (3 H, s), 1.19 (3 H, s), 1.4–1.7 (8 H), 1.60 (3 H, s), 1.68 (3 H, s), 1.8–2.0 (3 H), 2.20 (H, t, J = 7.6 Hz), 2.31 (H, q, J = 8.7 Hz), 5.11 (H, t, J = 6.8 Hz); ^{13}C NMR δ 17.5, 20.5, 22.9, 24.5, 25.7, 27.4, 32.2, 35.3, 39.1, 42.7, 44.2, 44.4, 79.2, 124.9, 131.0.

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.16; H, 11.70.

The minor isomer (**5hn**) showed the following: ^1H NMR δ 0.80–1.40 (2 H, m), 1.14 (3 H, s), 1.21 (3 H, s), 1.60 (3 H, s), 1.68 (3 H, s), 1.4–1.7 (6 H), 1.7–2.0 (3 H), 2.18 (H, t, J = 7.4 Hz), 2.38 (H, q, J = 7.7 Hz), 5.11 ', t, J = 6.8 Hz); ^{13}C NMR δ 17.6, 22.5, 24.1, 25.7, 27.2, 28.2, 32.6, 35.1, 36.7, 39.2, 42.3, 46.2, 79.2, 125.0, 131.0.

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.96; H, 11.73.

General Method for Rearrangement of Alcohols 5a–d. A mixture of alcohol and trifluoroacetic acid (90%, 10–12 mL for each mmol of alcohol) was boiled under reflux for 2–3 h. The reaction mixture was then cooled and the solvent removed by rotary evaporation. The dark brown residue was taken up in hexane (100 mL) and washed several times with water to remove trifluoroacetic acid. The trifluoroacetate could be purified if desired by flash column chromatography (3% ethyl acetate). However, generally it was suitably pure for subsequent hydrolysis (aqueous NaOH and MeOH, 1 h at room temperature). The MeOH solvent was then removed by rotary evaporation. The residue was taken up in ether and washed succesively with water, aqueous hydrochloric acid (10%), and brine. The organic solution was dried over $MgSO_4$. Removal of the solvent by rotary evaporation gave crude (usually solid) rearranged alcohol, which was then purified by flash column chromatography (15% ethyl acetate in hexane).

Rearrangement of *exo*-2,*endo*-3-Tetramethylenebicyclo-[3.2.0]heptan-*endo*-2-ol (*endo*-5b). The crude trifluoroacetate

was obtained as a light brown oil (84.8%): ^{1}H NMR δ 0.70–2.13 (15 H), 2.13–2.50 (H), 4.78 (H). The trifluoroacetate upon hydrolysis followed by purification by flash chromatography (15% ethyl acetate in hexane) gave two products. The major product, **1-*exo*,2-tetramethylenenorbornan-*syn*-7-ol (*exo*-6b)** (less polar, 89.9%), showed the following: mp 76–77 °C; ^{1}H NMR δ 0.88–1.96 (17 H), 3.71 (H, s); ^{13}C NMR δ 24.2, 25.4, 25.7, 30.1, 34.2, 37.0, 37.3, 41.3, 45.0, 85.4.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.23; H, 10.78.

A minor product, **1-*endo*,2-tetramethylenenorbornan-*syn*-7-ol (*endo*-6b)** (more polar, 2.8%), was obtained as an immobile oil which showed the following: ^{1}H NMR δ 0.7–0.9 (H, m), 1.00–1.98 (16 H), 3.70 (H, s); ^{13}C NMR δ 22.6, 25.2, 25.9, 26.4, 26.7, 29.7, 32.7, 38.8, 41.2, 47.6, 82.3.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.41; H, 10.83.

Rearrangement of *exo*-2,*endo*-3-Trimethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*endo*-5a). The purified trifluoroacetate was obtained by flash chromatography (hexane) in 75.5% yield: ^{1}H NMR δ 1.0–2.2 (13 H), 2.22–2.53 (H), 4.72 (H, m). The trifluoroacetate was hydrolyzed and the resulting alcohol purified by flash chromatography (15% ethyl acetate in hexane) to give 1-*exo*-2-trimethylenenorbornan-*syn*-7-ol (*exo*-**6a**) as a white solid (85%) which showed the following: mp 63–65 °C; ^{1}H NMR δ 1.18–1.25 (2 H, m), 1.25–2.00 (12 H), 2.12 H, br s), 3.60 (H, s); ^{13}C NMR δ 24.8, 25.3, 28.5, 31.9, 33.8, 35.9, 43.3, 48.7, 57.2, 82.1.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.49. Found: C, 78.88; H, 10.49.

Rearrangement of *exo*-2,*endo*-3-Pentamethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*endo*-5c). Flash chromatography (3% ethyl acetate in hexane) provided purified trifluoroacetate (84.5%) as an isomeric mixture. This mixture was hydrolyzed and then purified by flash chromatography (15% ethyl acetate in hexane) to give **1-*exo*,2-pentamethylenenorbornan-*syn*-7-ol (*exo*-6c)**: ^{1}H NMR δ 1.10–1.87 (18 H), 2.02 (H, br s), 3.48 (H, s); ^{13}H NMR δ 24.7, 24.8, 31.8, 32.0, 32.3, 34.9, 36.1, 38.2, 41.3, 46.4, 50.9, 83.0.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.08; H, 11.11.

A minor product, **1-*endo*,2-pentamethylenenorbornon-*syn*-7-ol (*endo*-6c)** was isolated (6.9%), which showed the following: ^{1}H NMR δ 0.84 (H, dd, J = 4.1, 11.4 Hz), 0.9–2.3 (18 H), 3.65 (H, s).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.03; H, 11.25.

Rearrangement of *exo*-2,*endo*-3-Hexamethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*endo*-5d). The crude trifluoroacetate was hydrolyzed to give the alcohols **6d**. The crude alcohols after preliminary purification by passage through a short plug of silica gel were separated by preparative HPLC (Partisil M20 10/50, 7% ethyl acetate in hexane, 12 mL/min) to give **1-*exo*,2-hexamethylenenorbornan-*syn*-7-ol (*exo*-6d)** (65.8%, t_r = 58 min), which showed the following: mp 101–102 °C; ^{1}H NMR δ 0.9–1.1 (21 H), 3.49 (H, s); ^{13}C NMR δ 24.7, 25.56, 26.59, 25.87, 26.1, 32.4, 32.6, 36.0, 40.2, 41.5, 44.1, 49.1, 86.4.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.49; H, 11.32.

A minor product, **1,*endo*-2-hexamethylenenorbornan-*syn*-7-ol (*endo*-6d)**, was isolated (17.2%, t_r = 70 min), which showed the following: ^{1}H NMR δ 0.84 (H, dd, J = 11, 19 Hz), 1.0–1.9 (18 H), 2.1–2.4 (2 H), 3.62 (H, s).

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.32, H, 11.32.

Rearrangement of *exo*-2,*exo*-3-Tetramethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*exo*-5b). The major product, **1,*exo*-2-tetramethylenenorbornan-*syn*-7-ol (*exo*-6b)** (75.5%), and minor product, **1,*endo*-2-tetramethylenenorbornan-*syn*-7-ol (*endo*-6b)** (2.1%), were obtained by the same procedure as described earlier for solvolysis of the exo-2,endo-3 isomer.

Rearrangement of *exo*-2,*exo*-3-Trimethylenebicyclo[3.2.0]heptan-*endo*-2-ol (*exo*-5a). A yield of 85% rearranged product **1,*exo*-2-trimethylenenorbornan-*syn*-7-ol (*exo*-6a)** was obtained by the same procedure as described earlier for solvolysis of the exo-2,endo-3 isomer.

Solvolysis of Alcohols 5e and 5f. To a cooled (ice bath) solution of bicyclo[3.2.0]heptan-2-ol (4.0 mmol) in THF (10 mL) was added sulfuric acid (40%, 5 mL) dropwise. After the addition was complete the cooling bath was removed and the reaction mixture allowed to stir 16 h. Then THF was removed by rotary evaporation (water aspirator) to give a semisolid. The residue was taken up in ether, washed with saturated sodium carbonate and then brine, and then dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (30 mm, 20% ethyl acetate in hexane) to give a crystalline white solid.

1,2,2-Trimethylbicyclo[2.2.1]heptan-*syn*-7-ol (6e). This compound was prepared from **5e** in 43% yield: mp 127–129 °C; ^{1}H NMR δ 0.95 (3 H, s), 0.96 (3 H, s), 1.07 (3 H, s), 1.00–1.28 (3 H), 1.46–1.73 (2 H), 1.82–2.0 (2 H), 2.13 (H, s), 3.70 (H, s); ^{13}C NMR δ 12.9, 24.3, 26.7, 29.1, 30.5, 36.7, 40.7, 44.8, 48.3, 85.2.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.01; H, 11.7.

1,7-Dimethylbicyclo[2.2.1]heptan-7-ol (6f). The alcohol **6f** was prepared from **5f** in 46.8% yield: mp 121–123 °C; ^{1}H NMR δ 0.86 (3 H, s), 1.17 (3 H, s), 1.10–2.00 (10 H); ^{13}C NMR δ 14.9, 18.2, 26.6, 27.6, 34.7, 35.6, 45.1, 45.3, 83.6.

M^+ Calcd for $C_9H_{16}O$: 140.1202. Found: 140.1224.

1,3,3-Trimethylbicyclo[2.2.1]heptan-*anti*-7-ol (6g). A solution of 2,6,6-trimethylbicyclo[3.2.0]heptan-2-ol (**5g**, 1.03 g, 6.7 mmol) in formic acid (20 mL) was heated at 90 °C for 4.5 h. The reaction mixture was cooled to room temperature, and water (25 mL) was added followed by extraction with ether (3 × 40 mL). The ether extracts were washed with brine and then dried over $MgSO_4$. Removal of the solvents gave crude product as a brown oil (0.73 g), which was further purified to give ***anti*-7-(formyloxy)-1,3,3-trimethylbicyclo[2.2.1]heptane** (0.55 g 45.2%) as a pale yellow liquid: ^{1}H NMR (60 MHz) δ 0.97 (6 H, s), 1.05 (3 H, s), 0.8–2.1 (7 H), 4.92 (H, s), 8.08 (H, s); ^{13}C NMR δ 18.1, 22.5, 27.0, 31.1, 32.3, 33.6, 46.5, 50.4, 50.5, 83.3, 161.0.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.30; H, 10.19.

A solution of *anti*-7-(formyloxy)-1,3,3-trimethylbicyclo[2.2.1]heptane in methanol (4 mL) and 15% aqueous sodium hydroxide (1 mL) was stirred at room temperature for 1 h. The solvent was removed by rotary evaporation, and the residue was dissolved in ether (100 mL). The ether solution was washed with 10% aqueous HCl and then dried over $MgSO_4$. Removal of the solvent gave an oil, which was purified by flash chromatography (20 mm, 10% ethyl acetate in hexane) to give **6g** as a colorless liquid (0.15 g, 68.2%), which solidified slowly: mp 44–45 °C; ^{1}H NMR (60 MHz) δ 0.8–2.05 (7 H), 0.94 (3 H, s), 0.98 (6 H, s), 1.86 (H, s), 3.95 (H, *br s*); ^{13}C NMR δ 18.0, 22.6, 27.3, 31.3, 31.7, 33.1, 46.9, 51.2, 52.5, 82.1.

M^+ Calcd for $C_{10}H_{18}O$: 154.1324. Found: 154.1287.

1,6,6-Trimethyl-2-oxabicyclo[2.2.2]octan-3-one (16e). A solution of 1,2,2-trimethylbicyclo[2.2.1]heptan-*syn*-7-ol (**6e**, 6.8 mmol) in dichloromethane (3 mL) was added to a suspension of pyridinium dichromate (3.76 g, 10 mmol) in dichloromethane (25 mL), and the reaction mixture was stirred for 24 h. The reaction mixture was diluted with dry ether (100 mL), stirred 5 min, and then allowed to sit 5 min. The supernatant solution was passed through a plug of silica gel. The residue was triturated with ether (2 × 15 mL), and the ether solution was passed through the silica gel plug. Solvent was removed by rotary evaporation, and the residual oil was purified by flash chromatography (10% ethyl acetate in hexane) to give **1,2,2-trimethylbicyclo[2.2.1]heptan-7-one (15e)** (73.8% yield), mp 130–135 °C; ^{1}H NMR δ 0.81 (3 H, s), 0.84 (3 H, s), 1.07 (3 H, s), 1.20–2.35 (7 H); ^{13}C NMR δ 9.9, 23.5, 24.6, 26.2, 28.3, 33.6, 40.2, 42.0, 47.2, 218.3. This ketone was converted into lactone **16e** without further purification.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.51; H, 9.74.

To a suspension of sodium bicarbonate (400 mg, 4.76 mmol) and *m*-chloroperoxybenzoic acid (800 mg, 4.6 mmol) in dichloromethane (20 mL) was added 1,2,2-trimethylbicyclo[2.2.1]heptan-7-one (**15e**, 1.45 mmol). After being stirred 24 h, the reaction mixture was filtered to remove *m*-chlorobenzoic acid and inorganic salts. The solids were washed with dichloromethane. Solvents were removed from the filtrate and washings by rotary evaporation. The residue was purified by flash chromatography (40 mm, 30% ethyl acetate in hexane) to give the lactone **16e** (91% yield): mp 159–161 °C; ^{1}H NMR δ 0.99 (3 H, s), 1.07 (3 H, s),

1.29 (3 H, s), 1.43–2.26 (6 H), 2.58 (H, m); ^{13}C NMR δ 19.9, 23.6, 25.9, 27.2, 29.0, 36.12, 36.16, 40.8, 86.4, 176.7.

1,*exo*-2-Trimethylenenorbornane (11a).[11] To a solution of alcohol *exo*-**6a** (0.1127 g, 0.74 mmol) in dichloromethane (15 mL) was added pyridinium dichromate (PDC, 0.386 g, 1.03 mmol) in one portion. Another 100 mg of PDC was added to the reaction mixture after 3 h and stirring continued for another 4 h. The reaction mixture was diluted with dry ether (60 mL), stirred for 5 min, and then allowed to sit for 5 min. The supernatant liquid was passed through a plug of silica gel. The residue was triturated with ether (2 × 15 mL) and the ether solution passed through the silica gel plug. Removal of the ether solvent by rotary evaporation (at 10 °C) gave crude ketone as a colorless oil (0.13 g), which was used for the next step without purification. The crude ketone was added to a solution of (*p*-tolylsulfonyl)hydrazine (0.186 g, 1 mmol) in absolute ethanol (3 mL). The reaction mixture was stirred at room temperature for 2 h. Solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (40 mm, 20% ethyl acetate in hexane) to give pure tosylhydrazone *exo*-**10a** as a white solid: mp 133–134 °C (82.4%); ^{1}H NMR δ 0.29–0.57 (H, m), 1.05–2.05 (12 H), 2.40 (3 H, s), 2.66 (H, t, *J* = 4 Hz), 6.92 (H, br s), 7.28 (2 H, d, *J* = 8.6 Hz), 7.80 (2 H, d, *J* = 8.2 Hz).

Anal. Calcd for $C_{17}H_{22}O_2NS$: C, 64.12; H, 6.96. Found: C, 64.30; H, 7.12.

A mixture of tosylhydrazone *exo*-**10a** (345 mg, 1.08 mmol), *p*-toluenesulfonic acid (50 mg), sodium cyanoborohydride (251 mg, 4 mmol), dimethylformamide (2.5 mL), and tetramethylene sulfone (2.5 mL) was heated for 21 h (oil bath temperature 110 °C). The reaction mixture was cooled to room temperature, diluted with water (10 mL), and extracted with hexane (40 mL). The hexane extract was washed successively with water (3 × 5 mL), aqueous sodium bicarbonate (5 mL), and brine and dried ($MgSO_4$). The hexane was removed by slow distillation at atmospheric pressure using a short vacuum-jacketed Vigreux column (6 in.) to afford **11a** in virtually quantitative yield. GC analysis (DC-7110, 11 ft, 150 °C) of the pale yellow oily product showed only one peak other than solvent. An analytical sample collected by preparative GC (DC-710, $^1/_4$ in. × 11 ft, 140 °C) showed the following: ^{1}H NMR δ 0.96 (H, dm, *J* = 9.3 Hz), 1.0–2.0 (14 H), 2.17 (H, br s); ^{13}C NMR δ 56.36, 47.95, 41.03, 39.89, 39.13, 33.61, 33.58, 29.48, 28.64, 26.46.

1,*exo*-2-Tetramethylenenorbornane (11b).[12] The crude ketone obtained by the oxidation of 1,*exo*-2-tetramethylenenorbornan-*syn*-7-ol (*exo*-**6b**) (0.188 g, 11.4 mmol), as for *exo*-**6a** above, with PDC (in CH_2Cl_2, 44 h) treated with (*p*-tolylsulfonyl)hydrazine in absolute ethanol (3 mL), and the reaction mixture was stirred for 2 h at room temperature. **1,*exo*-2-Tetramethylenenorbornan-7-one tosylhydrazone (*exo*-10b)** was isolated (79%) by flash chromatography (30 mm, 20% ethyl acetate in hexane) and showed the following: mp 151–152 °C; ^{1}H NMR δ 0.22 (H, apparent q, *J* = 11.8 Hz), 0.8–1.78 (13 H), 1.90 (H, d, *J* = 11.8 Hz), 2.40 (3 H, s), 2.58 (H, t, *J* = 4.3 Hz), 7.12 (1 H, br s), 7.28 (2 H, d, *J* = 8.3 Hz), 7.83 (2 H, d, *J* = 8.3 Hz).

Anal. Calcd for $C_{18}H_{24}O_2NS$: C, 65.03; H, 7.28. Found: C, 65.18; H, 7.37.

A mixture of tosylhydrazone **10b** (0.27 g, 0.81 mmol), *p*-toluenesulfonic acid (40 mg), sodium cyanoborohydride (220 mg, 3.5 mmol), dimethylformamide (2.5 mL), and tetramethylene sulfone (2.5 mL) was heated for 22 h in an oil bath (110 °C). The reaction mixture was worked up as described earlier for **11a** above to afford **11b** in virtually quantitative yield. An analytical sample isolated by preparative GC (DC-710, $^1/_4$ in. × 11 ft, 140 °C) showed the following: ^{1}H NMR δ 0.75 (H, dm, *J* = 9.3 Hz), 0.85–1.73 (16 H), 2.11 (H, t, *J* = 4.4 Hz); ^{13}C NMR δ 46.17, 41.90, 39.15, 38.18, 37.60, 37.45, 34.06, 31.42, 30.50, 26.39, 24.48.

1,*endo*-2-Tetramethylenenorbornan-7-one Tosylhydrazone (*endo*-10b). The crude ketone obtained by the oxidation of 1-*endo*-2-tetramethylenenorbornan-*syn*-7-ol (*endo*-**6b**) (9.8 mg, 0.06 mmol) as for *exo*-**6a** above with PDC in CH_2Cl_2 was directly treated with (*p*-tolylsulfonyl)hydrazine in absolute ethanol. The hydrazone *endo*-**10b** (13 mg, 61%) showed the following: mp 179 °C dec; ^{1}H NMR δ 0.92 (H, dd, *J* = 12.4, 7.4 Hz), 1.0–2.4 (15 H), 2.42 (3 H, s), 2.69 (H, t, *J* = 4.4 Hz), 7.29 (2 H, d, *J* = 8.3 Hz), 7.81 (2 H, d, *J* = 8.3 Hz).

Anal. Calcd for $C_{18}H_{24}O_2NS$: C, 65.03; H, 7.28. Found: C, 64.88; H, 7.08.

1,*exo*-2-Pentamethylenenorbornan-7-one Tosylhydrazone (*exo*-10c). Oxidation of *exo*-**6c** with PDC as for *exo*-**6a** above and reaction of the crude ketone with (*p*-tolylsulfonyl)hydrazine afforded *exo*-**10c** (80%), which showed: mp 171–173 °C; ^{1}H NMR δ 0.72–0.85 (2 H), 1.0–1.9 (H), 2.42 (3 H, s), 2.59 (H, t, *J* = 4.0 Hz), 6.92 (H, s), 7.30 (2 H, d, *J* = 8.3 Hz), 7.82 (2 H, d, *J* = 8.3 Hz).

Anal. Calcd for $C_{19}H_{26}O_2NS$: C, 65.86; H, 7.56. Found: C, 65.91; H, 7.57.

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Registry No. **3a**, 94-66-6; **3b**, 30079-93-7; **3d**, 38931-77-0; **3E**, 58105-24-1; *cis*-**4a**, 101544-57-4; *trans*-**4a**, 101544-58-5; *cis*-**4b**, 101544-55-2; *trans*-**4b**, 101544-56-3; *cis*-**4c**, 101544-59-6; *trans*-**4c**, 101544-60-9; *cis*-**4d**, 101544-61-0; *trans*-**4d**, 101544-62-1; **4g**, 78-70-6; **4h**, 7212-44-4; *endo*-**5a**, 101544-65-4; *exo*-**5a**, 101628-87-9; *endo*-**5b**, 101544-63-2; *exo*-**5b**, 101628-86-8; *endo*-**5c**, 101544-66-5; *endo*-**5d**, 101544-67-6; **5E**, 101544-68-7; **5F**, 101544-69-8; **5g**, 92471-17-5; **5hx**, 101544-70-1; **5hn**, 101628-88-0; *exo*-**6a**, 101544-74-5; *exo*-**6b**, 101544-72-3; *endo*-**6b**, 101628-89-1; *exo*-**6c**, 101544-76-7; *endo*-**6c**, 101628-91-5; *exo*-**6d**, 101544-78-9; *endo*-**6d**, 101628-92-6; **6E**, 101544-79-0; **6F**, 89243-96-9; **6g**, 101544-80-3; **7**, 101544-64-3; *exo*-**10a**, 101544-85-8; *exo*-**10b**, 101544-87-0; *endo*-**10b**, 101628-94-8; *exo*-**10c**, 101544-89-2; *exo*-**11a**, 49700-57-4; *exo*-**11b**, 36100-95-5; **15E**, 101544-83-6; **16E**, 101544-82-5; $(CuOTF)_2{\cdot}C_6H_6$, 37234-97-2; vinyl bromide, 593-60-2; 3,3-dimethylbicyclo[3.2.0]heptan-2-one, 71221-70-0; 1-methylbicyclo[3.2.0]heptan-2-one, 50459-43-3; *syn*-7-(trifluoroacetyl)-1,2-tetramethylenenorbornane, 101544-71-2; *sy*-7-(trifluoroacetyl)-1,2-trimethylenenorbornane, 101544-73-4; *syn*-7-(trifluoroacetyl)-1-*exo*-2-pentamethylenenornane, 101544-75-6; *syn*-7-(trifluoroacetyl)-1-*endo*-2-pentamethylenenorbornane, 101628-90-4; *syn*-7-(trifluoroacetyl)-1,2-hexamethylenenorbornane, 101544-77-8; *anti*-7-(formyloxy)-1,3,3-trimethylbicyclo[2.2.1]heptane, 101544-81-4; 1-*exo*-2-trimethylenenorbornan-7-one, 101544-84-7; 1-*exo*-2-tetramethylenenorbornan-7-one, 101544-86-9; 1-*endo*-2-tetramethylenenorbornan-7-one, 101628-93-7; 1-*exo*-2-pentamethylenenorbornan-7-one, 101544-88-1.