Intramolecular [2 + 2] Photocycloaddition of 2-(Alkenyloxy)cyclohex-2-enones

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Intramolecular photocycloaddition of 2-(2-propenyloxy)cyclohex-2-enones gave 2-oxabicyclo[2.1.1]hexane derivatives (head-to-tail adducts), and 2-(3-butenyloxy)cyclohex-2-enone afforded a 2-oxabicyclo[3.1.1]heptane derivative (a head-to-tail adduct) as the major product, along with a 2-oxabicyclo[3.2.0]heptane derivative (a head-to-head adduct). The structures were determined on the basis of spectroscopic data and an X-ray structure analysis. The skeletal rearrangements of the photoadducts to bicyclo[3.3.0]octane and bicyclo[3.2.1]octane ring systems are also described.

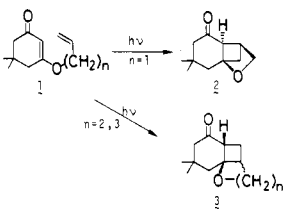
In recent years, the intramolecular [2 + 2] photocycloaddition of enones to olefins has been extensively used to synthesize a variety of interesting compounds including natural products.[1] We previously demonstrated that photochemical cycloaddition of 3-(alkenyloxy)cyclohex-2-enones (1) provides a simple route to the otherwise difficultly accessible 2-oxabicyclo[2.1.1] and -[*n*.2.0] ring systems **2**[2] and **3**[3] (Scheme I), depending upon the number of the methylene chains connecting two olefinic functions.[4] We have now planned to extend this reaction to 2-(alkenyloxy)cyclohex-2-enones. In this paper the photochemical behavior of 2-(2-propenyloxy)- (**5–7**) and 2-(3-butenyloxy)cyclohex-2-enones (**11**) and the transformation of the photoadducts to bicyclo[3.3.0]- and bicyclo[3.2.1]octane ring systems are described.[5]

Results and Discussion

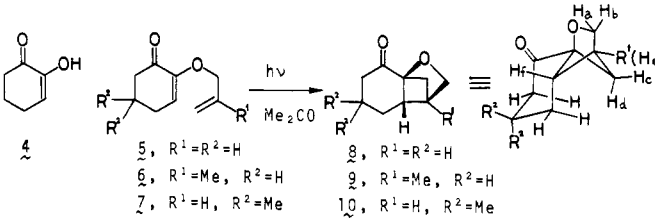
Photocycloaddition. The compounds **5**, **6**, and **11** were prepared in 74%, 34%, and 80% yields by refluxing 2-hydroxycyclohex-2-enone (**4**) with allyl alcohol, 2-methyl-2-propenol, and 3-butenol in benzene in the presence of *p*-toluenesulfonic acid, respectively. Compound **7** was prepared according to the reported procedure.[6]

A solution of **5** in acetone[7] was irradiated with a 350-W high-pressure mercury lamp through a Pyrex filter in a period of 2 h. The reaction was followed by TLC. After removal of solvent, the residue was chromatographed on silica gel to give a single photoadduct (**8**) in 57% yield.

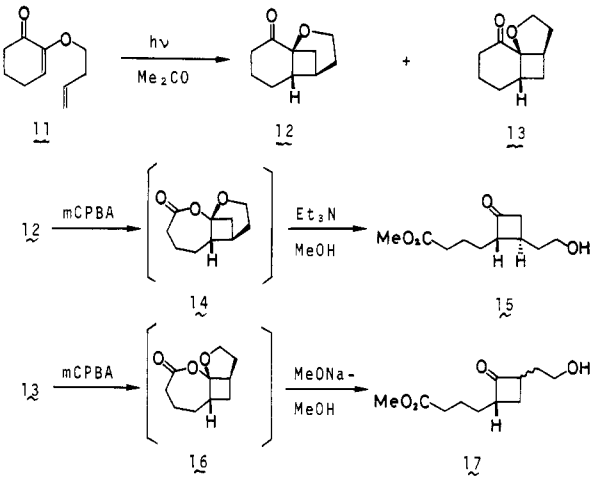
Scheme I



Scheme II



Scheme III



Compounds **6** and **7** were also irradiated in acetone to give **9** and **10** in 63% and 53% yields, respectively (Scheme II).

The structures of **8–10** were deduced from the spectroscopic evidence. For example, **8** showed strong carbonyl absorption at 1725 cm^{-1} in the IR spectrum (in CCl_4) for a saturated six-membered ketone. The distinguishing feature of the ^1H NMR spectrum of **8** was H_a and H_b which occurred at δ 3.84 and 3.93 as an AB quartet (J = 6 Hz). The ^1H NMR spectra, with the use of a shift reagent

(1) (a) Baldwin, S. W. In "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 123. (b) Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135.

(2) For the syntheses of the 2-oxabicyclo[2.1.1]hexane ring system, see: (a) Blanchard, E. P., Jr. U. S. Patent 3 342 785, 1967; *Chem. Abstr.* **1967**, *67*, 108316. (b) Farnum, D. G.; Mostashari, A. J. *Org. Prep. Proced. Int.* **1971**, *3*, 5.

(3) For the syntheses of 2-oxabicyclo[3.2.0]heptane ring systems, see: (a) Pomytkin, I. A.; Balenkova, E. S.; Anfilogova, S. N.; *Zh. Org. Khim.* **1982**, *18*, 532. (b) Murato, K.; Wolf, H. R.; Jeger, O. *Helv. Chim. Acta* **1981**, *64*, 215. (c) Kaupp, G.; Stark, M.; Fritz, H. *Chem. Ber.* **1978**, *111*, 3624. (d) Cantrell, T. S. *J. Org. Chem.* **1974**, *39*, 2242.

(4) (a) Tamura, Y.; Ishibashi, H.; Hirai, M.; Kita, Y.; Ikeda, M. *J. Org. Chem.* **1975**, *40*, 2702. (b) Ikeda, M.; Ohno, K.; Homma, K.; Ishibashi, H.; Tamura, Y. *Chem. Pharm. Bull.* **1981**, *29*, 2062. (c) Ikeda, M.; Ohno, K.; Takahashi, M.; Homma, K.; Uchino, T.; Tamura, Y. *Heterocycles* **1983**, *20*, 1005.

(5) A part of this work has appeared in a preliminary communication: Ikeda, M.; Takahashi, M.; Ohno, K.; Tamura, Y.; Kido, M. *Chem. Pharm. Bull.* **1982**, *30*, 2269.

(6) Ponaras, A. A. *Tetrahedron Lett.* **1980**, *21*, 4803.

(7) Irradiation of **5** in benzene in the presence of acetophenone gave a similar result. The reaction in benzene without acetophenone also proceeded but slowly.

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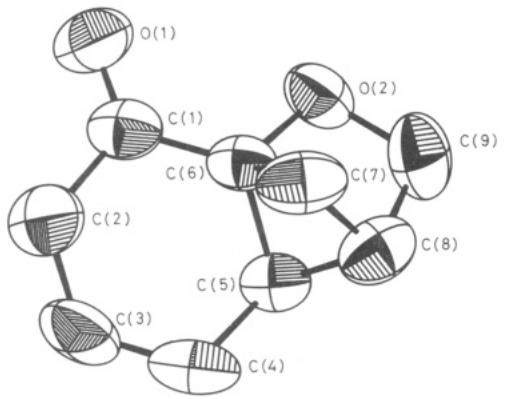


Figure 1. Perspective view of the molecule of 8.

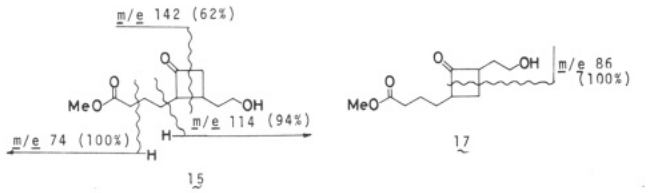


Figure 2. Major fragmentations in the mass spectra of **15** and **17**.

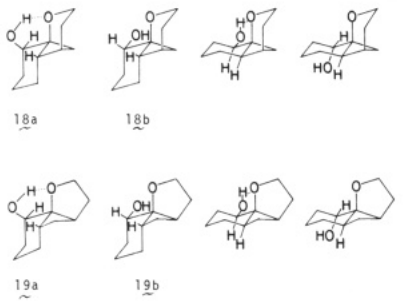
[Eu(fod)$_3$], and spin decoupling experiments revealed a large long-range coupling (J = 8 Hz) between H_c and H_f. Such coupling would occur only if these protons were in a W configuration in bicyclo[2.1.1]hexane.[8] Final confirmation of the structure was given by an X-ray structure analysis of **8** (Figure 1).

Irradiation of **11** in acetone gave a mixture of two isomeric products, which were separated by column chromatography on silica gel to give **12** (60%) and **13** (17%) (Scheme III).

The IR, ^{1}H NMR, and mass spectra of **12** and **13** were very similar (see Experimental Section). Differentiation of the structures **12** and **13** was made by transformation to the corresponding cyclobutanone derivatives **15** and **17**. Thus, Baeyer–Villiger oxidation of both **12** and **13** by *m*-chloroperoxybenzoic acid (MCPBA) gave the corresponding lactones **14** and **16**. Treatment of **14** with triethylamine in methanol afforded the cyclobutanone **15**, whereas the lactone **16** was found to be stable under the same conditions but, upon treatment with sodium methoxide in methanol, gave an inseparable 1:1 mixture of two isomeric cyclobutanones of **17**, presumably as a result of isomerization at the final stage. The distinguishing feature of the ^{1}H NMR spectra of **15** and **17** is the signal of the protons on the α-carbon atoms of the cyclobutanones which appeared between δ 2.4 and 3.2 (three protons) for **15** and between δ 3.0 and 3.5 (two protons) for **17**.[9] This observation is consistent with the presence of the hydroxyethyl group at the β-position in **15** and at the α-position in **17**. This result was further supported by the mass spectrum of **17** which showed the base peak at m/e 86, corresponding to $[O{=}C{=}CHCH_2CH_2OH]^+$ (see Figure 2).

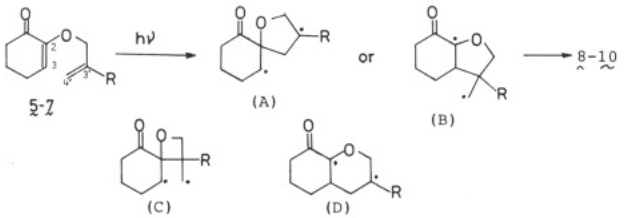
The stereochemistry of the adducts **12** and **13** was assigned from the following arguments. Reduction of **12** and **13** with sodium borohydride gave the isomeric pairs of the corresponding alcohols **18a,b** and **19a,b**. In the ^{1}H NMR spectra the signals of the proton on the carbon attached

Table I. Stereochemistry of Alcohols 18a,b and 19a,b



stereochemistry of OH	ax	eq	eq	ax
intramolecular hydrogen bonding	+	−	+	−

Scheme IV



to the hydroxyl group in **18a** and **19a** exhibited a considerably smaller coupling (a triplet-like signal, $J \approx 2$–4 Hz) compared with those (a doublet of doublets, J = 10–11 and 5–6 Hz) of **18b** and **19b**, suggesting that the hydroxyl group of the former two is axial and that of the latter two is equatorial. The IR spectra of **18a** and **19a** in a diluted carbon tetrachloride solution (0.01 M solution) showed a hydroxyl stretching frequency due to intramolecular hydrogen bonding between the hydroxyl group and the ether oxygen atom at 3580 cm^{-1}, whereas the isomers **18b** and **19b** showed only the unbonded absorption at 3620 cm^{-1}. Although four structures can be drawn for each series of the alcohols, depending upon the stereochemistry between the six- and four-membered rings,[10] an inspection of models reveals that the above results can be explained only when the six- and four-membered rings in **18a,b** and **19a,b** are cis-fused (Table I).

The intramolecular [2 + 2] photocycloaddition of one olefinic group to another may occur either in a head-to-head (parallel addition) or in a head-to-tail (cross addition) manner. It is well documented that the number of atoms connecting the two olefins is the most important factor in determining such regiochemical results of the intramolecular cycloaddition. Thus, in the 1,5-diene systems the preferred orientation is head-to-tail, while the head-to-head addition is favored in the 1,6-dienes. This has been explained by an empirical rule called "the rule of five";[11] the initial formation of the five-membered-ring biradical is preferred to other possible six-membered- or four-membered-ring biradicals in terms of strain and entropy factors. However, several exceptions for this rule have been reported,[11c,12] although the reasons for these exceptions are not clear in most cases.

(8) (a) Meinwald, J.; Lewis, A. *J. Am. Chem. Soc.* **1961**, *83*, 2769. (b) Wiberg, K. B.; Lowry, B. R.; Nist, B. J. *Ibid.* **1962**, *84*, 1594.
(9) Hoye, T. R.; Martin, S. J.; Peck, D. R. *J. Org. Chem.* **1982**, *47*, 331.
(10) In **19a,b** it is reasonable to assume that the tetrahydrofuran ring is cis fused to the cyclobutane ring.
(11) (a) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932. (b) Liu, R. S. H.; Hammond, G. S. *Ibid.* **1967**, *89*, 4936. (c) "The rule of five" in the carbonyl-substituted 1,5-dienes has been discussed in detail by Wolff and Agosta (Wolff, S.; Agosta, W. C. *Ibid.* **1983**, *105*, 1292, 1299).
(12) (a) Begley, M. J.; Mellor, M.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1979**, 235. (b) Margaretha, P. *Helv. Chim. Acta* **1976**, *59*, 2902. (c) Fröstl, W.; Margaretha, P. *Ibid.* **1976**, *59*, 2244. (d) Alder, A.; Niklaus, B.; Bellus, D. *Ibid.* **1982**, *65*, 2405.

Scheme V

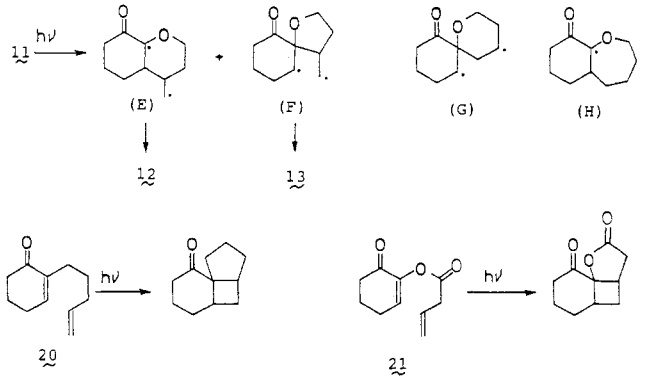
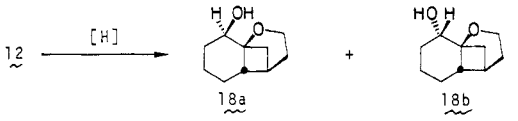


Table II. Reduction of 12



reducing agent	isolated yield, % 18a	18b	product ratio (%)[a] of 18a/18b
$NaBH_4$ in MeOH	15	76	27/73
$LiAlH_4$ in Et_2O	30	36	43/57
$LiAlH(O\text{-}t\text{-}Bu)_3$ in Et_2O	45	39	58/42
$LiBH_4$ in Et_2O	37	48	43/57

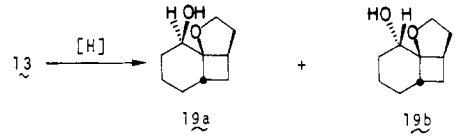
[a] Determined by GLC.

In the present study "the rule of five" can be nicely applied to the 2-(2-propenyloxy) derivatives **5–7** (see Scheme IV). In these cases the initial bond formation occurs between C(2)–C(4') or C(3)–C(3') to give five-membered biradical intermediates A or B, either of which may lead to the observed products **8–10**. The products derived from the four-membered biradical C (head-to-head adducts) or six-membered biradical D (head-to-head adducts or photo-Claisen products) were not detected.

Contrary to the prediction of "the rule of five", the 2-(3-butenyloxy) derivative **11** gave the head-to-head adduct **12** as the major product (Scheme V). This observation seems to point to a preference for forming six-membered biradical E or G over five-membered biradical F or seven-membered biradical H. Among them H, the most stable, and G are entropically disfavorable and would contibute little to the product distribution. One possible explanation for preference of E over F is radical stabilization of the former by the so-called "capto-dative substituent effect"[13] and thus the reaction proceeding through E can compete successfully with an alternative process involving entropically more favored but least stable F. In this connection, it is of interest to note that the closely related 2-(4-pentenyl)- (**20**)[14] and 2-(3-butenoyloxy)cyclohex-2-enones (**21**)[15] give exclusively head-to-head adducts. In these examples, no particular stabilizing effect in the six-membered biradicals can be expected, so that the reaction proceeds through a five-membered biradical, in accord with "the rule of five".

Rearrangement. In view of the fact that bicyclo[3.3.0]-[16] and -[3.2.1]octanes[17] are important as building blocks for syntheses of natural products, we have examined the solvolytic behavior of the mesylates derived from the photoadducts with the hope of discovering a new route to such ring systems.

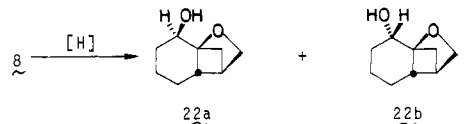
Table III. Reduction of 13



reducing agents	isolated yield, % 19a	19b	product ratio[a] of 19a/19b
$NaBH_4$ in MeOH	22	66	25/75
$LiAlH(O\text{-}t\text{-}Bu)_3$ in Et_2O	74	15	82/18
$LiBH_4$ in Et_2O	37	42	46/54

[a] Determined by GLC.

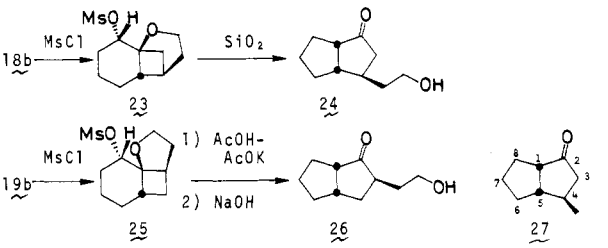
Table IV. Reduction of 8



reducing agent	isolated yield, % 22a	22b	product ratio[a] of 22a/22b
$NaBH_4$ in MeOH	16	53	24/76
$LiAlH(O\text{-}t\text{-}Bu)_3$ in Et_2O	68	14	83/17

[a] Determined by GLC.

Scheme VI



Each alcohol could be obtained as a major product by changing reducing reagents. Thus, sodium borohydride reduction of the ketones **8**, **12**, and **13** in methanol gave the equatorial alcohols **22b**, **18b**, and **19b** as the major products, whereas use of lithium tri-*tert*-butoxyaluminum hydride in ether afforded the axial alcohols **22a**, **18a**, and **19a** as the major products. The product ratios are shown in Tables II–IV. These alcohols could be mesylated by treatment with methanesulfonyl chloride in the presence of 4-(dimethylamino)pyridine (DMAP) and pyridine in methylene chloride at room temperature to give the corresponding mesylates.

The equatorial mesylate **23** underwent skeletal rearrangement simply by treating its benzene solution with silica gel to give ketone **24** in 70% yield (Scheme VI). The mesylate **25** was recovered unchanged under the above conditions but, upon heating in acetic acid in the presence

(13) Viehe, H. G.; Merényi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.
(14) Cargill, R. L.; Dalton, J. R.; O'Connor, S.; Michels, D. G. *Tetrahedron Lett.* **1978**, 4465.
(15) Ikeda, M.; Takahashi, M.; Uchino, T.; Tamura, Y. *Chem. Pharm. Bull.*, in press.
(16) For an example, see: Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820.
(17) For recent examples, see: (a) Yanagiya, M.; Kaneko, K.; Kaji, T.; Matsumoto, T. *Tetrahedron Lett.* **1979**, 1761. (b) Kende, A. S.; Roth, B.; Sanfilippo, P. J.; Blacklock, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5808. (c) Takada, K.; Shimono, Y.; Yoshii, E. *Ibid.* **1983**, *105*, 563.

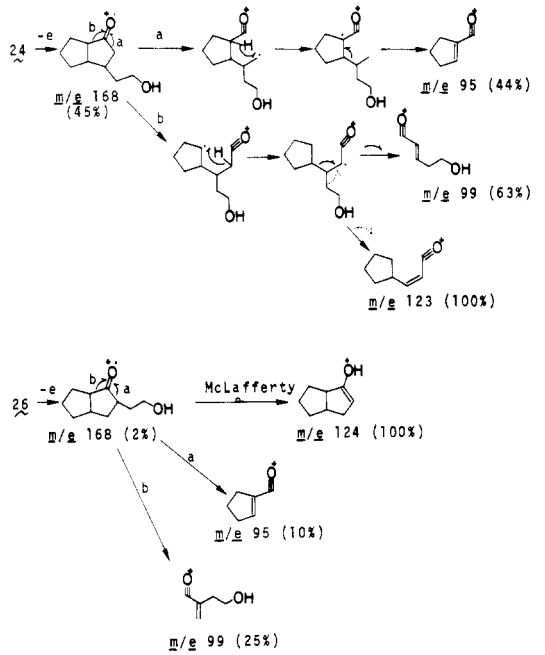


Figure 3. Major fragmentations in the mass spectra of **24** and **26**.

Table V. ^{13}C Chemical Schifts (in $CDCl_3$) of Bicyclo[3.3.0]octan-2-ones[a]

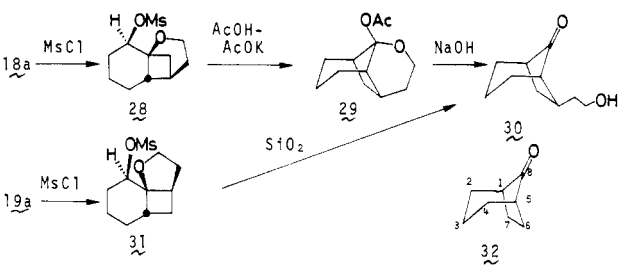
carbon	chemical shift, δ		
	27[b]	24	35
C-1	52.2	52.0	52.0
C-2	222.1	221.5	222.2
C-3	47.2	45.4	41.8
C-4	35.1	37.3	42.6
C-5	49.4	47.6	43.7
C-6	32.4	32.9	33.4
C-7	25.9	25.9	26.0
C-8	29.6	29.5	29.9
others	20.8 (CH_3)	39.0 (CH_2CH_2OH)	65.9 (CH_2OH)
		61.2 (CH_2CH_2OH)	

[a] The δ values are in parts per million downfield from Me_4Si. [b] Taken from ref 18.

of potassium acetate at 110 °C followed by alkaline hydrolysis, gave isomeric ketone **26** in 74% yield. The structures of two ketones **24** and **26** were elucidated by the spectroscopic evidence. The IR spectra of **24** and **26** showed absorption at 1740 and 1730 cm^{-1}, respectively, typical of a five-membered ketone, in addition to absorption due to hydroxyl group. That the carbonyl band of the latter appeared at lower frequency than that of the former is attributed to the intramolecular hydrogen bonding. The important fragmentations in the mass spectra of **24** and **26** are summarized in Figure 3. One distinguishing feature of the mass spectrum of **26** is a peak at m/e 124, which arises by a McLafferty rearrangement. Confirmation of structure **24** was made by comparison of ^{13}C NMR spectrum with that of 4-methylbicyclo[3.3.0]-octan-2-one (**27**,[18] Table V).

In sharp contrast, when the axial mesylate **28** was heated in acetic acid in the presence of potassium acetate at 110 °C, the acetate **29** was obtained (Scheme VII). Alkaline hydrolysis of **29** gave bicyclo[3.2.1]octanone **30** in 68% overall yield. Interestingly, the mesylate **31** was rather unstable, and when its benzene solution was passed through silica gel column, it afforded the same ketone **30**

Scheme VII



Scheme VIII

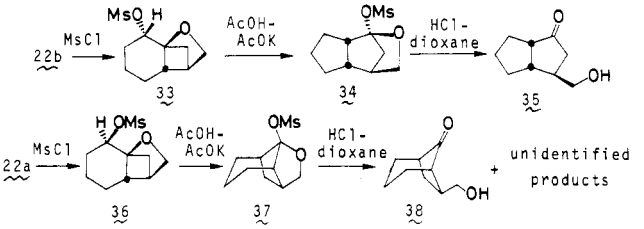


Table VI. ^{13}C Chemical Shifts (in $CDCl_3$) of Bicyclo[3.2.1]octan-8-ones[a]

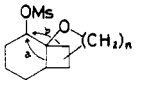
carbon	chemical shift, δ		
	32[b]	30	38
C-1	44.9	45.6	45.7
C-2	37.1	36.7	36.6
C-3	17.4	17.8	17.9
C-4	37.1	36.7	36.9
C-5	44.9	51.4	48.8
C-6	22.6	32.5	38.6
C-7	22.6	30.9	26.9
C-8	222.9	222.1	221.6
others		40.2 (CH_2CH_2OH)	66.5 (CH_2OH)
		60.4 (CH_2CH_2OH)	

[a] The δ values are in parts per million downfield from Me_4Si. [b] Taken from ref 19.

in 72% yield. The ketone showed a strong carbonyl band at 1745 cm^{-1} (five-membered ketone) and hydroxyl absorption at 3650 and 3450 cm^{-1} in the IR spectrum. The assignment of the structure **30** was made by comparison of the ^{13}C NMR spectrum (Table VI) with that of bicyclo[3.2.1]octan-8-one (**32**)[19] and consideration of the fact that the same ketone **30** was produced from both **28** and **31**.

Heating the equatorial mesylate **33** in acetic acid in the presence of potassium acetate at 110 °C gave **34** in 91% yield (Scheme VIII), whereas the axial mesylate **36**, under the same conditions, afforded **37** in 90% yield. The structures of **34** and **37** were ascertained by conversion to bicyclo[3.3.0]octanone **35** and bicyclo[3.2.1]octanone **38**, respectively, whose structures were readily assigned on the basis of comparison of their mass spectra and ^{13}C NMR spectra (Tables V and VI) with those of **24** and **30**.

In summary, the equatorial mesylates migrate by bond a to give a bicyclo[3.3.0]octane ring system whereas the



axial mesylates migrate by bond b to give a bicyclo-[3.2.1]octane ring system. These specific rearrangements are in good agreement with a concerted mechanism which involves an antiperiplanar conformation of the migrating

(18) Whitesell, J. K.; Matthew, R. S. *J. Org. Chem.* **1977**, *42*, 3878.

(19) Heumann, A.; Kolshorn, H. *J. Org. Chem.* **1979**, *44*, 1575.

C–C bond and the leaving group.

Experimental Section

All melting points are uncorrected. ^1H NMR spectra were determined with a Hitachi R-22 (90 MHz) spectrometer (tetramethylsilane as an internal standard), and ^{13}C NMR spectra were obtained by Fourier transformation carried out on a Hitachi R-900 spectrometer at 22.6 MHz. IR spectra were recorded with a JASCO IRA-1 spectrophotometer and UV spectra with a Hitachi 124 spectrophotometer. High- and low-resolution mass spectra were obtained with a JMS-D-300 instrument at 70 eV. GLC was performed on a Shimadzu GC-4B gas chromatograph (nitrogen as carrier gas; 2 m × 3 mm column packed with 5% SE-30 at 120 °C). Photoirradiation was carried out in an immersion well through a Pyrex filter for a large-scale experiment and in a Pyrex tube for a small-scale experiment by using an Eikosha 350-W high-pressure mercury lamp.

2-(2-Propenyloxy)cyclohex-2-enone (5). A solution of **4** (1.05 g, 9.65 mmol) and allyl alcohol (0.72 g, 12.4 mmol) in benzene (20 mL) containing *p*-toluenesulfonic acid (50 mg) was refluxed for 5 h with a Dean–Stark water separator. The reaction mixture was washed with 10% NaOH solution and brine, dried ($MgSO_4$), and concentrated to give **5** (1.06 g, 74%) as a colorless oil, which was essentially pure and used for the next step without further purification: IR (liquid film) 1670, 1620 cm^{-1}; UV (EtOH) 260 nm (log ϵ 3.80); ^1H NMR ($CDCl_3$) δ 1.8–2.6 (m, 6), 4.28 (dt, 2, J = 5, 1.5 Hz, $CH_2CH{=}CH_2$), 5.1–5.45 (m, 2, $CH_2CH{=}CH_2$), 5.86 (t, 1, J = 4 Hz, 3-H), 5.94 (ddt, 1, J = 17, 10, 5 Hz, $CH_2CH{=}CH_2$); mass spectrum, m/e 152 (M^+). Analysis was carried out by high-resolution mass spectrometry: calcd for $C_9H_{12}O_2$, 152.0835; found, 152.0829.

2-[(2-Methyl-2-propenyl)oxy]cyclohex-2-enone (6). By use of a procedure similar to that described for **5**, **6** (500 mg, 34%) was obtained from **4** (1.0 g, 9.1 mmol) and 2-methyl-2-propenol (920 mg, 12.8 mmol) as a colorless oil: IR (liquid film) 1680, 1625 cm^{-1}; UV (EtOH) 260 nm (log ϵ 3.69); ^1H NMR ($CDCl_3$) δ 1.76 (s, 3, CH_3), 1.85–2.6 (m, 6), 4.20 (br s, 2, $CH_2CMe{=}CH_2$), 4.9–5.05 (m, 2, $CH_2CMe{=}CH_2$), 5.98 (t, 1, J = 4 Hz, 3-H); mass spectrum, m/e 166 (M^+). Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.1003.

(1*RS*,6*RS*,7*SR*)-9-Oxatricyclo[5.2.1.0^{1,6}]decan-2-one (8). A solution of **5** (100 mg, 0.66 mmol) in acetone (10 mL) was irradiated for 2 h under a nitrogen atmosphere. The solvent was removed, and the residual liquid was submitted to column chromatography (silica gel, benzene–ethyl acetate, 4:1) to give **8**: 57 mg (57%); mp 64–65 °C [from ether–petroleum ether (bp 30–60 °C)]; IR (CCl_4) 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4–2.4 (m, 8), 2.75–2.95 (m, 1), 2.87 (s, 1, H_e), 3.84, 3.93 (AB q, 1 each, J = 6 Hz, H_a and H_b); ^1H NMR [after addition of Eu(fod)$_3$ (100 mg) to a solution of **8** (17 mg) in $CDCl_3$ (0.4 mL)] δ 7.58 (d, 1, J_{de} = 2 Hz, H_e), 8.82 (t, 1, $J_{cd} = J_{cf}$ = 8 Hz, H_c), 9.88 (dd, 1, J_{cd} = 8 Hz, J_{de} = 2 Hz, H_d), 11.6 (m, 1, H_f), 12.79 (d, 1, J_{ab} = 7 Hz, H_a or H_b), 13.08 (d, 1, J_{ab} = 7 Hz, H_b or H_a); mass spectrum, m/e 152 (M^+). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.04; H, 8.10.

(1*RS*,6*RS*,7*SR*)-7-Methyl-9-oxatricyclo[5.2.1.0^{1,6}]decan-2-one (9). A solution of **6** (160 mg, 9.6 mmol) in acetone (16 mL) was irradiated for 1.5 h, and the workup yielded **9**: 101 mg (63%); colorless oil; IR (CCl_4) 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 3, CH_3), 1.4–2.5 (m, 8), 2.58 (d, 1, J = 8 Hz, H_d), 3.60, 3.71 (AB q, 1 each, J = 6 Hz, H_a and H_b); ^1H NMR [after addition of Eu(fod)$_3$ (52 mg) to a solution of **9** (11 mg) in $CDCl_3$ (0.4 mL)] δ 8.95 (t, 1, $J_{cd} = J_{cf}$ = 8 Hz, H_c), 9.76 (d, 1, J_{cd} = 8 Hz, H_d), 11.7 (m, 1, H_f), 12.79, 13.26 (AB q, 1 each, J_{ab} = 7 Hz, H_a and H_b); mass spectrum, m/e 166 (M^+). Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.0992.

(1*RS*,6*RS*,7*SR*)-4,4-Dimethyl-9-oxatricyclo[5.2.1.0^{1,6}]decan-2-one (10). A solution of **7** (730 mg, 4.1 mmol) in acetone (73 mL) was irradiated for 2 h, and the workup yielded **10**: 390 mg (53%); mp 75.5–76 °C [from petroleum ether (bp 30–60 °C)]; IR (CCl_4) 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90, 1.12 (s each, 3 each, $2CH_3$), 1.7–2.6 (m, 6), 2.7–2.85 (m, 1), 2.82 (s, 1, H_e), 3.84, 3.93 (AB q, 1 each, J = 6 Hz, H_a and H_b); ^1H NMR [after addition of Eu(fod)$_3$ (150 mg) to a solution of **10** (18 mg) in $CDCl_3$ (0.45 mL)] δ 7.43 (d, 1, J_{de} = 2 Hz, H_e), 8.12 (t, 1, $J_{cd} = J_{cf}$ = 8 Hz, H_c), 9.85 (m, 1, H_d), 11.98, 12.12 (AB q, 1 each, J_{ab} = 6 Hz, H_a and H_b), 12.55 (m, 1, H_f). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.13; H, 9.09.

2-(3-Butenyloxy)cyclohex-2-enone (11). By use of a procedure similar to that described for **5**, **11** (7.2 g, 80%) was prepared from **4** (6.0 g, 54 mmol) and 3-butenol (4.0 g, 56 mmol) as an oil: IR (liquid film) 1690, 1620 cm^{-1}; UV (EtOH) 260 nm (log ϵ 3.61); ^1H NMR δ ($CDCl_3$) 1.65–2.6 (m, 8), 3.70 (t, 2, J = 6.5 Hz, OCH_2), 4.85–5.15 (m, 2, $CH_2CH{=}CH_2$), 5.55–6.05 (m, 2, $CH_2CH{=}CH_2$ and 3-H); mass spectrum, m/e 166 (M^+). Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.0994.

(1*RS*,6*RS*,7*SR*)-10-Oxatricyclo[5.3.1.0^{1,6}]undecan-2-one (12) and (1*RS*,6*SR*,8*RS*)-11-Oxatricyclo[6.3.0.0^{1,6}]undecan-2-one (13). A solution of **11** (2.3 g, 13.9 mmol) in acetone (230 mL), flushed with nitrogen, was irradiated under a stream of nitrogen for a period of 1.5 h. After removal of the solvent, the residual oil was submitted to column chromatography (silica gel; ethyl acetate–benzene, 1:4). The fast-moving fraction gave **13**: 400 mg (17%); mp 44.5–46 °C [from petroleum ether (bp 30–60 °C)]; IR (KCl) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4–2.9 (m, 11), 2.96 (br q, 1, J = 6 Hz), 3.95–4.45 (m, 2, OCH_2); mass spectrum, m/e 166 (relative intensity) (M^+, 100), 138 (11), 125 (8), 112 (48), 110 (15), 84 (16), 70 (8), 55 (13). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.94; H, 8.61.

The slow-moving fraction gave **12**: 1.38 g (60%); mp 63–63.5 °C [from petroleum ether (bp 30–60 °C)]; IR (KCl) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.6 (m, 11), 2.78 (dd, 1, J = 11, 6 Hz, 11-H), 4.11 (dt, 1, J = 11, 6.5 Hz, 9-H), 4.28 (dt, 1, J = 11, 7.5 Hz, 9-H); mass spectrum, m/e (relative intensity) 166 (M^+, 41), 138 (26), 125 (75), 112 (87), 110 (28), 96 (47), 84 (40), 70 (64), 67 (52), 55 (100). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.84; H, 8.48.

Methyl 4-[2,3-*trans*-3-(2-Hydroxyethyl)-1-oxocyclobut-2-yl]butanoate (15). A solution of **12** (106 mg, 0.64 mmol) and *m*-chloroperoxybenzoic acid (121 mg, 0.70 mmol) in dry methylene chloride (5 mL) was stirred at room temperature for 30 min and diluted with benzene (30 mL). The solution was washed with 10% Na_2SO_3, 10% Na_2CO_3, and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed (silica gel; ethyl acetate–benzene, 1:4) to give a lactone **14** (96 mg) as an oil, which was directly used for the next step. A solution of **14** (96 mg) and triethylamine (0.2 mL) in methanol (10 mL) was stirred at room temperature for 30 min. After removal of the solvent, the residual oil was chromatographed (silica gel; ethyl acetate–benzene, 2:3) to give **15**: 98 mg (72% from **12**); oil; IR (CCl_4) 3640, 3500, 1780, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45–2.4 (m, 9), 2.12 (s, 1, OH), 2.4-3.2 (m, 3, $CHCOCH_2$), 3.64 (s, 3, OCH_3), 3.68 (t, 2, J = 6 Hz, OCH_2); mass spectrum, m/e (relative intensity) 214 (M^+, 10), 197 (16), 183 (35), 142 (62), 123 (26), 114 (94), 110 (81), 99 (38), 94 (50), 81 (66), 74 (100). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.87; H, 8.64.

Methyl 4-[4-(2-Hydroxyethyl)-1-oxocyclobut-2-yl]butanoate (17, as a Stereoisomeric Mixture). A solution of **13** (36 mg, 0.22 mmol) and *m*-chloroperoxybenzoic acid (41 mg, 0.24 mmol) in dry methylene chloride (3.5 mL) was stirred at room temperature for 3.5 h and diluted with benzene (30 mL). The solution was washed with 10% Na_2SO_3, 10% Na_2CO_3, and brine and dried ($MgSO_4$). After removal of the solvent, the residual oil was dissolved in dry methanol (4 mL), and sodium methoxide (9.5 mg) was added. The mixture was stirred at room temperature for 10 min under a nitrogen atmosphere. The mixture was neutralized with 10% HCl, diluted with water, and extracted with chloroform. The extract was washed with brine, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed (silica gel; ethyl acetate–benzene, 2:3) to give **17** (35 mg, 77%) as an oily mixture of two stereoisomers (ca. 1:1, checked by GLC): IR (CCl_4) 3470, 1765, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.05 (m, 7), 2.2–2.6 (m, 3), 2.5 (br, 1, OH), 3.0–3.5 (m, 2, $CHCOCH$), 3.55–3.8 (m, 2, OCH_2), 3.65 (s, 3, OCH_3); mass spectrum, m/e (relative intensity) 183 (M – CH_3O, 10), 114 (64), 97 (23), 86 (100), 74 (17), 55 (72). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.87; H, 8.64.

(1*RS*,2*SR*,6*RS*,7*SR*)- and (1*RS*,2*RS*,6*RS*,7*SR*)-10-Oxatricyclo[5.3.1.0^{1,6}]undecan-2-ol (18a and 18b). (A) By Sodium

Borohydride. Sodium borohydride (70 mg, 1.8 mmol) was added portionwise to a solution of **12** (300 mg, 1.8 mmol) in methanol (15 mL) with stirring at 0 °C over 10 min. The mixture was stirred for 30 min and concentrated. The residue was diluted with water and extracted with chloroform. The extract was washed with brine, dried ($MgSO_4$), and concentrated to give a mixture of two products, which were separated by column chromatography (silica gel; ethyl acetate–benzene, 1:4). The fast-moving fraction gave **18a**: 45 mg (15%); oil; IR (CCl_4) 3580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.5 (m, 12), 2.71 (s, 1, OH), 3.54 (br s, 1, 2-H), 4.11 (t, 2, J = 6 Hz, 9-H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.34; H, 9.94.

The slow-moving fraction gave **18b**: 233 mg (76%); oil; IR (CCl_4) 3620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–2.45 (m, 12), 2.94 (s, 1, OH), 3.40 (dd, 1, J = 11, 6 Hz, 2-H), 3.85–4.35 (m, 2, 9-H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.22; H, 9.86.

(B) By Lithium Aluminum Hydride. To a suspension of lithium aluminum hydride (19 mg, 0.5 mmol) in dry ether (4 mL) was added dropwise a solution of **12** (85 mg, 0.5 mmol) in dry ether (4 mL) at 0 °C. The mixture was stirred at room temperature for 10 min and usual workup gave **18a** (26 mg, 30%) and **18b** (31 mg, 36%).

(C) By Lithium Tri-*tert*-butoxyaluminum Hydride. To a suspension of lithium tri-*tert*-butoxyaluminum hydride (580 mg, 2.3 mmol) in dry ether (13 mL) was added dropwise a solution of **12** (310 mg, 1.9 mmol) in dry ether (12 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min, and the workup gave **18a** (140 mg, 45%) and **18b** (120 mg, 39%).

(D) By Lithium Borohydride. To a stirred solution of **12** (52 mg, 0.31 mmol) in ether (5 mL) was added portionwise lithium borohydride (7 mg, 0.31 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min, and the workup gave **18a** (19 mg, 37%) and **18b** (25 mg, 48%).

(1*RS*,2*RS*,6*SR*,8*RS*)- and (1*RS*,2*SR*,6*SR*,8*RS*)-11-Oxatricyclo[6.3.0.0^{1,6}]undecan-2-ol (19a and 19b). (A) By Sodium Borohydride. The ketone **13** (180 mg, 1.1 mmol) was reduced with sodium borohydride (41 mg, 1.1 mmol) in the same manner as that described for the reduction of **12**. Workup and chromatography (silica gel; ethyl acetate–benzene, 1:4) gave two isomeric alcohols. The fast-moving fraction gave **19a**: 40 mg (22%); oil; IR (CCl_4, 0.01 M solution) 3580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.45 (m, 11), 2.65 (br s, 1, OH), 2.71 (br q, 1, J = 6 Hz), 3.55–3.65 (m, 1, 2-H), 4.09 (dd, 2, J = 8, 5 Hz, 10-H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.60; H, 9.71.

The slow-moving fraction gave **19b**: 120 mg (66%); oil; IR (CCl_4, 0.01 M solution) 3620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.4 (m, 11), 2.17 (s, 1, OH), 2.97 (br q, 1, J = 7 Hz), 3.72 (dd, 1, J = 11, 6 Hz, 2-H), 3.85–4.3 (m, 2, 10-H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.06; H, 9.86.

(B) By Lithium Tri-*tert*-butoxyaluminum Hydride. To a suspension of lithium tri-*tert*-butoxyaluminum hydride (370 mg, 1.5 mmol) in dry ether (5 mL) was added a solution of **13** (120 mg, 0.73 mmol) in dry ether (5 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min, and the workup gave **19a** (91 mg, 74%) and **19b** (19 mg, 15%).

(C) By Lithium Borohydride. To a stirred solution of **13** (162 mg, 0.98 mmol) in ether (10 mL) was added portionwise lithium borohydride (21 mg, 0.98 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min, and the workup gave **19a** (61 mg, 37%) and **19b** (70 mg, 43%).

(1*RS*,2*SR*,6*RS*,7*SR*)- and (1*RS*,2*RS*,6*RS*,7*SR*)-9-Oxatricyclo[5.2.1.0^{1,6}]decan-2-ol (22a and 22b). (A) By Sodium Borohydride. The ketone **8** (300 mg, 2.0 mmol) was reduced with sodium borohydride (74 mg, 2.0 mmol) in the same manner as that described for the reduction of **12**. Workup and chromatography (silica gel; ethyl acetate–*n*-hexane, 1:1) gave **22a** (50 mg, 16%) from the fast-moving fraction and **22b** (161 mg, 53%) from the slow-moving fraction.

Compound **22a** was an oil: IR (CCl_4) 3595, 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–2.2 (m, 8), 2.22 (dd, 1, J = 8, 3 Hz, 10-H), 2.54 (s, 1, OH), 2.66 (d, 1, J = 3 Hz, 7-H), 3.78 (s, 2, 8-H), 3.99 (br s, 1, 2-H). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.61; H, 9.28.

Compound **22b** was an oil: IR (CCl_4), 3605, 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.1 (m, 8), 2.22 (dd, 1, J = 8, 3 Hz, 10-H), 2.66 (d, 1, J = 3 Hz, 7-H), 3.15 (br s, 1, OH), 3.78 (s, 2, 8-H), 3.6–3.9 (m, 1, 2-H). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.05; H, 9.15.

(B) By Lithium Tri-*tert*-butoxyaluminum Hydride. The ketone **8** (150 mg, 1.0 mmol) was reduced with lithium tri-*tert*-butoxyaluminum hydride (300 mg, 1.5 mmol) in the same manner as that described for the reduction of **12**. The workup gave **22a** (103 mg, 68%) and **22b** (20 mg, 14%).

(1*RS*,4*SR*,5*RS*)-4-(2-Hydroxyethyl)bicyclo[3.3.0]octan-2-one (24). To a solution of **18b** (85 mg, 0.5 mmol), DMAP (7 mg), and pyridine (490 mg) was added methanesulfonyl chloride (74 mg, 0.6 mmol), and the mixture was stirred at room temperature for 10 h. Water (0.5 mL) was added, and the mixture was stirred for 10 min. The mixture was washed with 10% HCl, saturated $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated to give the crude mesylate **23** (116 mg, 93%) which was used directly for the next reaction. A portion of this was purified by recrystallization: mp 85–86 °C [*n*-hexane–petroleum ether (bp 30–60 °C); IR (CCl_4) 1365, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–2.5 (m, 12), 3.03 (s, 3, CH_3), 3.9–4.4 (m, 2, OCH_2), 4.31 (dd, 1, J = 11, 6 Hz). Anal. Calcd for $C_{11}H_{18}O_4S$: C, 53.64; H, 7.37. Found: C, 53.44; H, 7.44.

The mesylate **23** (116 mg) was dissolved in benzene (15 mL), and silica gel (10 g) was added. After being stirred at room temperature for 48 h, the mixture was filtered, and the filtrate was concentrated. The residue was chromatographed (silica gel; ethyl acetate–benzene, 2:3) to give **24**: 55 mg (70%); oil; IR (CCl_4) 3650, 3460, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.9 (m, 13), 2.21 (s, 1, OH), 3.66 (t, 2, J = 6 Hz); mass spectrum, m/e (relative intensity) 168 (M^+, 45), 150 (11), 123 (100), 99 (63), 95 (44). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.26; H, 9.75.

(1*RS*,3*SR*,5*RS*)-3-(2-Hydroxyethyl)bicyclo[3.3.0]octan-2-one (26). A solution of **19b** (47 mg, 0.28 mmol), DMAP (20 mg, 0.16 mmol), pyridine (190 mg), and methanesulfonyl chloride (370 mg, 3.2 mmol) was stirred at room temperature for 15 h. Workup gave the mesylate **25**: 63 mg (92%); mp 55–56 °C (from ether–*n*-hexane); IR (CCl_4) 1370, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–2.45 (m, 11), 2.95 (s, 3, CH_3), 2.9–3.25 (m, 1), 3.85–4.2 (m, 2, OCH_2), 4.52 (dd, 1, J = 12, 7 Hz). Anal. Calcd for $C_{11}H_{18}O_4S$: C, 53.64; H, 7.37; S, 13.02. Found: C, 53.84; H, 7.55; S, 13.07.

The mesylate **25** (63 mg) and potassium acetate (50 mg) were dissolved in acetic acid (5 mL), and the mixture was heated at 110 °C (bath temperature) for 8 h. After evaporation of acetic acid in vacuo, ether (20 mL) was added. The solution was washed with brine, saturated $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated. The residue was dissolved in methanol (6 mL) containing 10% NaOH (3 drops), and the mixture was stirred at room temperature for 1 h. After concentration, water was added, and the mixture was extracted with chloroform. The extract was washed with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed (silica gel; ethyl acetate–benzene, 1:4) to give **26**: 32 mg (74%); oil; IR (CCl_4) 3450, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.9 (m, 13), 2.7 (br, 1, OH), 3.6–3.8 (m, 2); mass spectrum, m/e (relative intensity) 169 ($M + 1$, 5), 168 (M^+, 2), 151 (5), 124 (100), 99 (25), 95 (10), 83 (82). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.29; H, 9.92.

***exo*-7-(2-Hydroxyethyl)bicyclo[3.2.1]octan-8-one (30). (A) From 18a.** A solution of **18a** (142 mg, 0.85 mmol), pyridine (490 mg), DMAP (50 mg), and methanesulfonyl chloride (370 mg, 3.2 mmol) in dry methylene chloride (5 mL) was stirred at room temperature for 48 h. Water was added, the mixture was stirred vigorously for 1 h, and the organic layer was washed with 10% HCl, saturated $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated to give the mesylate **28**: 195 mg (93%); mp 37–37.5 °C [from *n*-hexane–petroleum ether (bp 30–60 °C)]; IR ($CHCl_3$) 1350, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15–2.5 (m, 12), 3.02 (s, 3, CH_3), 4.07 (t, 2 H, J = 6 Hz, OCH_2), 4.45–4.55 (m, 1). Anal. Calcd for $C_{11}H_{18}O_4S$: C, 53.64; H, 7.37. Found: C, 53.63; H, 7.47.

A solution of **28** (104 mg, 0.42 mmol) and potassium acetate (70 mg) in acetic acid (7 mL) was heated at 110 °C (bath temperature) for 10 h. The workup and chromatography (silica gel; ethyl acetate–*n*-hexane, 1:3) gave **29**: 65 mg; oil; IR (CCl_4) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.4 (m, 12), 2.06 (s, 3, $COCH_3$), 2.6 (br, 1), 3.78 (ddd, 1, J = 11.5, 8, 4 Hz), 4.15 (ddd, 1, J = 15, 8, 7 Hz). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.59; H, 8.78.

Table VII. Bond Distances (in Angstroms) and Bond Angles (in Degrees) Involving Nonhydrogen Atoms with Estimated Standard Deviation in Parentheses for Compound 8

Distances

O(1)-C(1)	1.210 (5)	O(2)-C(6)	1.441 (4)
O(2)-C(9)	1.462 (6)	C(1)-C(2)	1.521 (6)
C(1)-C(6)	1.489 (6)	C(2)-C(3)	1.524 (7)
C(3)-C(4)	1.520 (7)	C(4)-C(5)	1.529 (6)
C(5)-C(6)	1.559 (6)	C(5)-C(8)	1.558 (6)
C(6)-C(7)	1.572 (6)	C(7)-C(8)	1.531 (6)
C(8)-C(9)	1.534 (7)		

Angles

C(6)-O(2)-C(9)	99.2 (3)	O(1)-C(1)-C(2)	122.1 (4)
O(1)-C(1)-C(6)	125.2 (4)	C(2)-C(1)-C(6)	112.8 (4)
C(1)-C(2)-C(3)	112.8 (4)	C(2)-C(3)-C(4)	113.0 (4)
C(3)-C(4)-C(5)	108.0 (4)	C(4)-C(5)-C(6)	111.7 (3)
C(4)-C(5)-C(8)	119.6 (4)	C(6)-C(5)-C(8)	80.5 (3)
C(2)-C(6)-C(1)	115.5 (3)	O(2)-C(6)-C(5)	103.5 (3)
O(2)-C(6)-C(7)	102.5 (3)	C(1)-C(6)-C(5)	119.0 (3)
C(1)-C(6)-C(7)	123.9 (4)	C(5)-C(6)-C(7)	87.6 (3)
C(6)-C(7)-C(8)	80.9 (3)	C(5)-C(8)-C(7)	89.1 (3)
C(5)-C(8)-C(9)	98.4 (4)	C(7)-C(8)-C(9)	98.2 (4)
O(2)-C(9)-C(8)	102.0 (4)		

A portion of this (38 mg, 0.18 mmol) was dissolved in methanol (3 mL) containing 10% NaOH (3 drops), and the mixture was heated at 30–40 °C for 2 h. After evaporation of the solvent, water was added, and the mixture was extracted with chloroform. The extract was washed with brine, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed (silica gel; ethyl acetate–*n*-hexane, 3:2) to give **30**: 27 mg (68% from **28**); oil; IR (CCl_4) 3650, 3450, 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4–2.4 (m, 13), 1.67 (s, 1, OH), 3.63 (t, 2, J = 6 Hz, OCH_2); mass spectrum, m/e (relative intensity) 168 (M^+, 77), 123 (65), 95 (42), 93 (44), 81 (71), 79 (58), 67 (100). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: 71.44; H, 9.67.

(B) From 19a. A solution of **19a** (53 mg, 0.32 mmol), pyridine (240 mg), DMAP (25 mg), and methanesulfonyl chloride (300 mg, 2.6 mmol) in methylene chloride (5 mL) was stirred at room temperature for 48 h. Water (0.1 mL) was added, and the mixture was stirred for 1 h. The mixture was washed with 10% HCl, saturated $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed (silica gel; ethyl acetate–*n*-hexane, 1:1) to give **30** (39 mg, 72%) as an oil.

(1*RS*,2*SR*,6*SR*,7*RS*)-8-Oxatricyclo[5.2.1.0^{2,6}]decan-7-yl Methanesulfonate (34). To a solution of **22b** (102 mg, 0.66 mmol), pyridine (490 mg), and DMAP (73 mg) in dry methylene chloride (5 mL) was added methanesulfonyl chloride (230 mg, 2.0 mmol), and the mixture was stirred at room temperature for 10 h. The workup and column chromatography (silica gel; ethyl acetate–*n*-hexane, 1:1) gave the mesylate **33**: 111 mg (72%); IR ($CHCl_3$) 1360, 1175 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.2 (m, 8), 2.31 (dd, 1, J = 8, 3 Hz, 10-H), 2.72 (d, 1, J = 3 Hz, 7-H), 3.11 (s, 3, CH_3), 3.80 (s, 2, 8-H), 4.68 (dd, 1, J = 10, 6 Hz, 2-H).

The mesylate **33** (58 mg, 0.25 mmol) was dissolved in acetic acid (2 mL) and potassium acetate (98 mg) was added. The mixture was heated at 110 °C for 10 h and then concentrated. Chloroform was added, and the organic layer was washed with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated to give **34**: 53 mg (91%); mp 53.5–54 °C [from petroleum ether (bp 30–60 °C)]; IR ($CHCl_3$) 1365, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.75 (m, 11), 3.14 (s, 3, CH_3), 3.62 (d, 1, J = 7 Hz), 3.99 (dd, 1, J = 7, 3 Hz). Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.70; H, 6.94. Found: C, 51.77; H, 6.91.

(1*RS*,4*SR*,5*RS*)-4-(Hydroxymethyl)bicyclo[3.3.0]octan-2-one (35). A solution of **34** (177 mg, 0.76 mmol) in dioxane (2 mL) and 10% HCl (2 mL) was heated at 110 °C for 5 h. The mixture was diluted with water (30 mL) and extracted with chloroform. The extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed (silica gel; ethyl acetate–*n*-hexane, 3:1) to give **35**: 70 mg (60%); oil; IR (CCl_4) 3650, 3450, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.75 (m, 11), 1.98 (s, 1, OH), 3.64 (d, 2, J = 5 Hz); mass spectrum, m/e (relative intensity) 154 (M^+, 63), 123 (100), 95 (68), 85 (43), 79 (37), 67 (93). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.25; H, 9.30.

(1*RS*,3*RS*,7*SR*,8*RS*)-9-Oxatricyclo[5.3.0.0^{3,8}]decan-8-yl Methanesulfonate (37). To a solution of **22a** (45 mg, 0.29 mmol), pyridine (240 mg), and DMAP (32 mg) in dry methylene chloride (2 mL) was added methanesulfonyl chloride (101 mg, 0.88 mmol), and the mixture was stirred at room temperature for 10 h. Workup and chromatography (silica gel; ethyl acetate–*n*-hexane, 1:1) gave the mesylate **36**: 48 mg (70%); oil; IR ($CHCl_3$) 1350, 1175 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–2.2 (m, 8), 2.29 (dd, 1, J = 8, 3 Hz, 10-H), 2.69 (d, 1, J = 3 Hz, 7-H), 3.08 (s, 3, CH_3), 3.77 (s, 2, 8-H), 4.85–5.0 (m, 1, 2-H).

The mesylate **36** (31 mg, 0.13 mmol) was dissolved in acetic acid (2 mL), and potassium acetate (52 mg) was added. The mixture was stirred at 110 °C for 10 h. The workup gave **37**: 28 mg (90%); oil; IR ($CHCl_3$) 1365, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.1 (m, 8), 2.2–2.65 (m, 3), 3.17 (s, 3, CH_3), 3.62 (d, 1, J = 6 Hz), 3.95–4.1 (m, 1). Anal. Calcd for $C_{11}H_{16}O_4S$: C, 51.70; H, 6.94; S, 13.80. Found: C, 51.77; H, 6.87; S, 13.33.

6-*exo*-6-(Hydroxymethyl)bicyclo[3.2.1]octan-8-one (38). A solution of **37** (35 mg, 0.15 mmol) in dioxane (1 mL) and 10% HCl (1 mL) was heated at 110 °C for 3 h. Workup and chromatography (silica gel; ethyl acetate–*n*-hexane, 2:1) gave **38** (9 mg, 38%) and unidentified products (14 mg).

Compound **38** was an oil: IR (CCl_4) 3640, 3450, 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15–2.4 (m, 11), 1.76 (br, 1, OH), 3.39 (dd, 1, J = 10, 6 Hz), 3.49 (dd, 1, J = 10, 6 Hz); mass spectrum, m/e (relative intensity) 154 (M^+, 34), 123 (100), 95 (42), 93 (19), 79 (21), 67 (43). Analysis was carried out by high-resolution mass spectrometry: calcd for $C_9H_{14}O_2$, 154.0991; found, 154.0980.

X-ray Analysis of Compound 8. Crystal Data: $C_9H_{12}O_2$, mol wt 152; monoclinic, a = 7.984 (4) Å, b = 12.047 (5) Å, c = 8.843 (3) Å, β = 105.27 (3)°, Z = 4, d_{exptl} = 1.23 g cm^{-3}; space group $P2_1/n$; MoKα radiation; μ(MoKα) = 20.9 cm^{-1}.

Data Collection. The crystal data and intensity data were derived from the measurements on a Syntex R_3 four-circle diffractometer with graphite-monochromated MoKα radiation. Intensity data were collected on the diffractometer with the same radiation by using an ω–2θ scanning technique within 2θ less than 45°. Three reference reflextions monitored periodically showed no significant intensity fluctuations during the course of data collection. A total of 707 were used for the structure analysis. Intensities were corrected for Lorenz and polarization factors but not for absorption.

Structure Determination and Refinement. The structure was solved by a direct method (MULTAN method).[20] The positional coordinates were refined by the block-diagonal least-squares method, by using anisotropic temperature factors for all the nonhydrogen atoms and isotopic ones for the hydrogen atoms. The final R value was 0.059. The atomic scattering factors were taken from the literature.[21] Bond lengths and bond angles are listed in Table VII.

Registry No. **4**, 10316-66-2; **5**, 83505-28-6; **6**, 86433-25-2; **7**, 77426-39-2; **8**, 87391-84-2; **9**, 87318-74-9; **10**, 87318-75-0; **11**, 87318-76-1; **12**, 87318-77-2; **13**, 87318-78-3; **15**, 87318-79-4; **17** (isomer 1), 87318-80-7; **17** (isomer 2), 87336-02-5; **18a**, 87318-81-8; **18b**, 87391-85-3; **19a**, 87318-82-9; **19b**, 87391-86-4; **22a**, 87336-03-6; **22b**, 87392-47-0; **23**, 87318-83-0; **24**, 87318-84-1; **25**, 87392-48-1; **26**, 87318-85-2; **28**, 87391-87-5; **29**, 87318-86-3; **30**, 87318-87-4; **31**, 87318-88-5; **33**, 87336-04-7; **34**, 87318-89-6; **35**, 87318-90-9; **36**, 87392-49-2; **37**, 87318-91-0; **38**, 87318-92-1; DMAP, 1122-58-3; $NaBH_4$, 16940-66-2; $LiAlH_4$, 16853-85-3; $LiAlH(O\text{-}t\text{-}Bu)_3$, 17476-04-9; $LiBH_4$, 16949-15-8; allyl alcohol, 107-18-6; 2-methyl-2-propenol, 513-42-8; 3-butenol, 627-27-0.

Supplementary Material Available: Tables of observed and calculated structure factors, atomic coordinates, and thermal parameters (7 pages). Ordering information is given on any current masthead page.

(20) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(21) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. IV, p 71.