meric alcohols **32**. Analysis by glpc (3% Carbowax, 8 ft × 0.125 in., 120°, 25 cc/min of He) showed two peaks in a ratio of *ca.* 2:1. The mixture of carbinols was purified by preparative glpc (20% XF-1150, 10 ft × 0.125 in., 130°, 100 cc/min of He). Carbinols **32** have δ (CCl_4) 3.73 and 3.68 (doublets, J = 2.2 and 2.0 Hz, respectively, relative areas *ca.* 2:1, respectively, carbinol), 1.15, 1.12 (pair of equally intense singlets), and 1.07, 1.03 (pair of equally intense singlets, the former pair having *ca.* twice the area of the latter pair, methyls). The high resolution mass spectrum of **32** exhibits m/e 162.1040 (calcd for $C_{11}H_{14}O$: 162.1045).[20]

Registry No.—**3**, 28256-69-1; **4**, 28256-70-4; **5**, 28256-71-5; **6**, 28256-72-6; **7**, 28256-73-7; **8**, 28256-74-8; **9**, 28256-75-9; **10**, 28256-76-0; **12**, 28256-77-1; **17**, 28256-78-2; **18**, 28256-79-3; **19**, 25995-00-0; **21**, 25995-02-2; **22**, 26121-77-7; **25**, 28256-82-8; **31**, 28256-83-9; **32a**, 28256-84-0; **32b**, 28256-85-1.

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[20] We thank Dr. D. M. Rosenthal and Mr. F. Williams, Research Triangle Institute, for the high-resolution mass spectrum.

The Photochemistry of Bicyclo[6.1.0]nonanones[1a]

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The solution photochemistry of three bicyclic ketones containing formally nonconjugated chromophores in a medium ring has been examined. Bicyclo[6.1.0]nonan-3-one (1) affords *trans*-5,8-nonadienal (4), 2-allylcyclohexanone (5), and 3-vinylcycloheptanone (6). Photolysis in methanol also gives methyl 8-nonenoate (7). In addition to photoreduction to the corresponding alcohols, bicyclo[6.1.0]nonan-4-one (2) forms aldehydes **15** and **16** and ester **17**. A distinct solvent effect on the product distribution was observed in this system. 4,5-Epoxycyclooctanone (3) undergoes simple photoreduction of the ketone function. These results are discussed in relation to similar systems.

As part of a continuing study[2,3] on the photochemical interaction of formally nonconjugated chromophores contained within the same molecule, we have examined the photochemistry of the modified cyclooctanones **1–3**. Compound **1** is the cyclopropyl analog of the β,γ-unsaturated ketone, 3-cyclooctenone, upon which we have reported earlier.[2] The remaining ketones are functionalized in the γ,δ position with a cyclopropane and an epoxide unit. These compounds can be considered as derivatives of 4-cyclooctenone.[3] These specific systems have been chosen in a search for photochemical interplay of remote functional groups, since the medium-ring framework provides the geometrical proximity which has been effective in inducing transannular processes.[4]

Bicyclo[6.1.0]nonan-3-one.—The synthesis of **1** was accomplished from 3-cyclooctenol[5] by the sequence: acetylation, Simmons–Smith reaction, saponification, and chromic acid oxidation. Acetylation was critical to this synthetic scheme since the Simmons–Smith method failed on the alcohol itself. The ultraviolet spectrum of **1** suggests weak interaction of the cyclopropyl moiety with the carbonyl group as evidenced by an enhancement of the extinction coefficient [uv max (hexane) 289 nm (ϵ 44)]. This spectrum is similar to that of 3-cyclooctenone [292 nm (ϵ 47)][2] for which some overlap of the two π bonds seems certain.[6] The ability of a cyclopropane to function in this fashion has only recently been documented.[7]

Irradiation of **1** leads to the rapid formation of three major products in approximately a 1:2:1 ratio in either benzene or cyclohexane. Photoisomer **4** displays spectroscopic properties (detailed in the Experimental Section) which suggest the presence of aldehyde, terminal vinyl, and a nonconjugated trans-disubstituted double bond. The relative position of the double bonds is evidenced by a doubly allylic methylene group at δ 2.7 in the nmr. The carbon skeleton of this compound was shown by the isolation of *n*-nonanal from a photolysis mixture which had subsequently been catalytically hydrogenated. 2-Allylcyclohexanone (**5**) was identified by comparison with a synthetic sample derived from allyl Grignard addition to cyclohexene oxide and subsequent chromic acid oxidation of the resulting alcohol. The structure of **6** rests on spectral data which show a cycloheptanone carbonyl (5.90 μ) and a terminal vinyl group. The absence of a signal at *ca.* δ 3.0 (CH_2=CHCHCO) in the nmr indicates that the vinyl substituent is not adjacent to the carbonyl group,[2] and, therefore, the presence of an important fragment at m/e 81 in the mass spectrum of **6** establishes the indicated locus of the vinyl substituent.[8]

Irradiation of **1** in methanol solvent gave methyl 8-nonenoate (**7**) in addition to the above three products. Methyl ester and terminal vinyl groups were manifest spectroscopically, and catalytic hydrogenation converted **7** to methyl *n*-nonanoate.

Examination of the photoisomers under the irradiation conditions demonstrated the absence of interconversion. In fact, except for aldehyde **4** which decomposed to an unidentified material of short retention time, the products were surprisingly stable to the photolysis conditions.

These results parallel closely those obtained by Heck-

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[1] (a) Supported by a research grant from the National Science Foundation; (b) Alfred P. Sloan Research Fellow, 1968–1970; (c) NDEA Title IV Predoctoral Fellow, 1965–1968; NSF Trainee, 1968–1969.

[2] J. K. Crandall, J. P. Arrington, and J. Hen, *J. Amer. Chem. Soc.*, **89**, 6208 (1967).

[3] J. K. Crandall, J. P. Arrington, and R. J. Watkins, *Chem. Commun.*, 1052 (1967).

[4] A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev., Chem. Soc.*, **20**, 119 (1966).

[5] J. K. Crandall, D. B. Banks, R. A. Colyer, R. J. Watkins, and J. P. Arrington, *J. Org. Chem.*, **33**, 423 (1968).

[6] R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

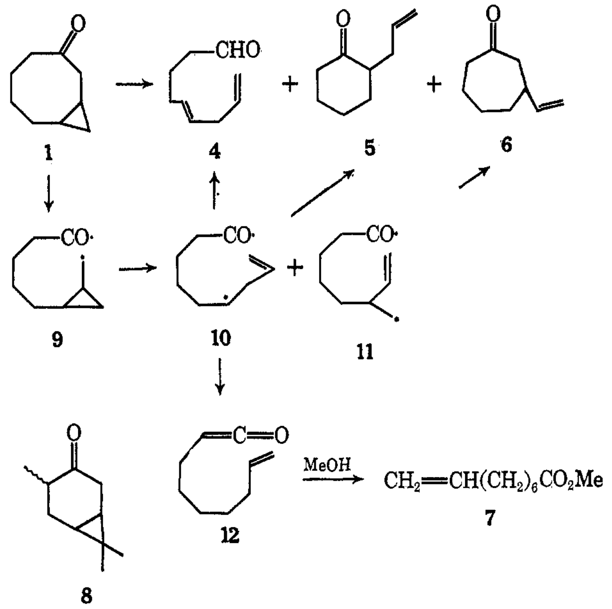
[7] A recent report describes the uv spectra of **1** and its trans isomer: K. B. Wiberg and A. deMeijere, *Tetrahedron Lett.*, 59 (1969).

[8] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 3.

ert and Kropp[9] in their study of the isomeric 4-caranones (**8**), which are smaller ring analogs of **1**. A related rationale can be applied to the transformations of **1** as illustrated below. Excitation of **1** is followed by virtually exclusive α cleavage in the direction to yield diradical **9**. This selective ring fission is attributed to the delocalizing ability of the cyclopropyl substituent[10] which apparently exerts itself effectively in the transition state for bond rupture of electronically excited **1**. In this regard, **1** parallels the behavior of its double bond analog.[2] Once generated the cyclopropylcarbinyl radical moiety is postulated to readily unravel in a well-established manner[11] to produce isomeric biradicals **10** and **11**. Radical coupling processes from these intermediates give cyclic ketones **5** and **6**, respectively. Alternatively, **10** can partake of favorable six-center hydrogen transfers to give aldehyde **4** and ketene **12**, the precursor of ester **7**. The absence of products from ketene **12** in benzene and cyclohexane is probably only a reflection of the propensity of this reactive intermediate to take part in further thermal and photochemical decomposition under conditions where it is not rendered inert by reaction with the solvent.

One aspect of this photochemical system which differs from that of 3-cyclooctenone is the lack of interconversion of the ketone products or their reversion to starting material. In principle, α cleavage of **5** and **6** in the correct manner would regenerate the postulated biradical intermediates **10** and **11**, respectively. These transients should interconvert *via* the cyclopropylcarbinyl intermediate **9** in view of the known chemistry of homoallylic radical species.[11] The observed photostability of **5** and **6** relative to **1** can be attributed to an especially efficient decomposition of **1**, an exceptionally inefficient α cleavage for **5** and **6**, or both. Ordinarily, a certain degree of reversibility of the α-cleavage step appears to obtain in the photolysis of saturated ketones,[12] thereby decreasing the efficiency of observed reaction. In the case of **1**, the propensity of the cyclopropylcarbinyl radicals to spring open could promote more judicious utilization of the initial diradical derived from α cleavage. Inefficiency in the photolysis of **5** and **6** may result from a special route for relaxation of the excited states of these ketones, namely intramolecular energy transfer from the carbonyl group to the double bond. Such an explanation had been advanced previously to account for exceptional photostability of γ,δ-unsaturated ketones (Scheme I).[13]

SCHEME I



Bicyclo[6.1.0]nonan-4-one.—This ketone was prepared by two different routes, each of which utilized 1,5-cyclooctadiene as the starting material. Simmons–Smith reaction followed by the oxymercuration–reduction procedure[14] for hydration gave a mixture of epimeric alcohols **13** and **14** which were smoothly converted to ketone **2** by chromic acid oxidation. Alternatively, the epimeric mixture of alcohols could be obtained from 4-cyclooctenol[5] by the sequence: acetylation, Simmons–Smith reaction, and saponification. As before, masking of the alcohol function was critical for the success of the cyclopropanation step. The ultraviolet spectrum of **2** [uv max (hexane) 287 nm (ϵ 15)] was normal for saturated cycloalkanones.[15]

The photochemistry of **2** was markedly dependent upon the solvent utilized. In benzene only slow decomposition without the formation of characterizable products was observed. Photolysis in cyclohexane or isopropyl alcohol resulted in reduction to the epimeric alcohols. In methanol, however, a more complex product mixture was obtained. The products were 3-(*cis*-2-allylcyclopropyl)propanal (**15**), 4-(*cis*-2-vinylcyclopropyl)butanal (**16**), methyl 3-(*cis*-2-propylcyclopropyl)propanoate (**17**), alcohols **13** and **14**, starting ketone, and an unidentified material in the ratio of 20:3:25:15:36:1.

Structure **15** was assigned on the basis of spectral data which show an aldehyde, a terminal vinyl group, cyclopropyl protons, and methylene groups adjacent to both aldehyde (δ 2.45) and vinyl (δ 2.0) functions.[16] Double resonance experiments confirm these assignments which distinguish between the two probable structures **15** and **16** since only the former possesses an allylic methylene group. Retention of the cis stereochemistry at the cyclopropyl ring is confirmed by the observation of two multiplets (δ 0.75 and -0.2) for the cyclopropyl methylene group. The trans isomer should give a single absorption for the methylene protons.[17]

The structural assignment for **16** is considered tentative owing to the small amount of this material obtained. The nmr spectrum was quite similar to that

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[9] D. C. Heckert and P. J. Kropp, *J. Amer. Chem. Soc.*, **90**, 4911 (1968). See also M. S. Carson, W. Cocker, S. M. Evans, and P. V. R. Shannon, *Tetrahedron Lett.*, 6153 (1968); R. G. Carlson and E. L. Biersmith, *Chem. Commun.*, 1049 (1969).

[10] J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, **91**, 1877, 1879 (1969).

[11] L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 6556 (1967), and earlier papers in this series.

[12] P. J. Wagner and R. W. Spoerke, *ibid.*, **91**, 4437 (1969).

[13] L. D. Hess, J. L. Jacobson, K. Schaffner, and J. N. Pitts, Jr., *ibid.*, **89**, 3684 (1967).

[14] H. C. Brown and P. Geoghegan, Jr., *ibid.*, **89**, 1522 (1967).

[15] Cyclooctanone, for example, exhibits a uv max (EtOH) at 283 nm (ϵ 17): N. J. Leonard and F. H. Owens, *ibid.*, **80**, 6039 (1958).

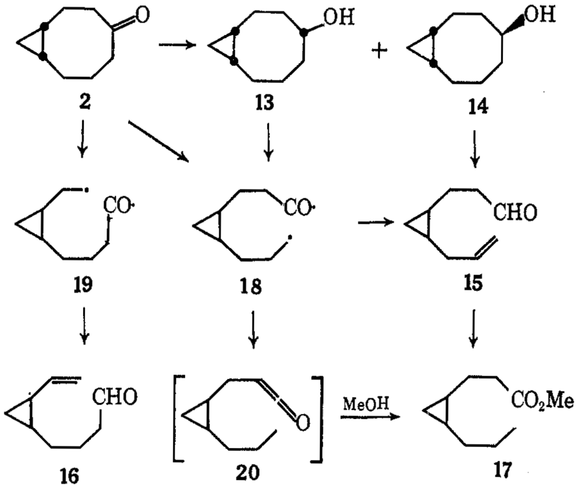
[16] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, pp 181–183.

[17] L. K. Montgomery, personal communication of unpublished results, 1969; D. T. Longone and A. H. Miller, *Chem. Commun.*, 447 (1967), and references therein.

of **15** except for a simplified pattern in the olefinic region.

The assignment of structure **17** follows from the presence of a methyl ester, cyclopropyl protons, and an aliphatic methyl group. The carbon skeleton was shown to be the same as **15** by transforming this latter compound to **17** by the sequence: catalytic hydrogenation, chromic acid oxidation, and diazomethane esterification (Scheme II).

SCHEME II



The alcohol product was homogeneous to all gc conditions utilized but was readily recognized as an epimeric mixture by the presence of two nonintegral signals for the carbinol hydrogen in the nmr at δ 4.0 and 3.5. Conversion of the mixture to the trimethylsilyl ethers allowed for the separation and characterization of the two products. Examination of molecular models suggests that the cis isomer has available reasonably good conformations which place the carbinol hydrogen in the plane of the cyclopropyl ring where it can experience deshielding from the magnetic anisotropy of the cyclopropyl ring.[18] The isomer whose signal appears at δ 4.0 is thus assigned as **13**. The trans epimer **14** appears to be more or less uninfluenced by the cyclopropyl ring, and its carbinol proton (δ 3.5) is similar to the analogous hydrogen in cyclooctanol (δ 3.65). The silyl ethers show a similar effect. The ratio of **13** to **14** from the photolysis is 3:1, whereas lithium aluminum hydride reduction of ketone **2** gives a 7:1 ratio.

The gross aspects of the photochemistry of **2** appear to be quite typical of simple cycloalkanones. Reduction of the carbonyl function to an alcohol by hydrogen abstraction from the solvent is a well-established process, as is transformation to acyclic aldehydes and esters (*via* the corresponding ketenes). Intermediate biradicals **18** and, to a much lesser extent, **19** serve as suitable reactive species which can undergo further transformations leading to the observed products. The large preference for reaction *via* **18** over **19** is striking. However, interpretation of this fact in terms of a special effect of the cyclopropyl group appears to be unwarranted in view of a similar discrimination in the case of 3-methylcyclohexanone.[12] In both instances the preferred product is derived from bond cleavage on the side of the carbonyl group farther from the substituent. The potential reversibility of the α-cleavage step could be utilized to rationalize these results,[12] but clearly more information is required before an adequate explanation for the effects of substituents on these cleavage reactions can be tendered. Nonetheless, it should be noted that relatively subtle structural changes are apparently capable of markedly influencing the course of cycloalkanone photoisomerizations.

A second noteworthy point arises from the pronounced solvent effect which leads to competition between bimolecular reduction and α cleavage in methanol, but only the former in cyclohexane or isopropyl alcohol. A plausible explanation for this novel observation is that in methanol the carbonyl group is surrounded by oriented solvent molecules which retard bimolecular hydrogen atom abstraction from the methyl group of the solvent. This allows for competitive α cleavage. On the other hand, in cyclohexane the bare carbonyl function experiences little difficulty in abstracting hydrogen from the solvent, and reduction predominates. According to this view, isopropyl alcohol, which hydrogen bonds less effectively than methanol and offers a better hydrogen abstraction reaction, behaves more like cyclohexane than methanol. The factors which determine the relative efficiencies for α cleavage *vs.* reduction for a given ketone are poorly understood, but further studies on solvent effects are indicated. The potential control of these competitive pathways has important implications for synthetic uses.[19]

4,5-Epoxycyclooctanone.—Epoxide **3** was obtained from peracid oxidation of 4-cyclooctenone. The ultraviolet spectrum gave no evidence for transannular interaction between the epoxide and ketone functions: uv max (hexane) 288 nm (ϵ 13).

Assessment of the photochemical behavior of **3** was complicated by the propensity of the initially formed photoproduct mixture to undergo further nonphotochemical transformation. Thus, irradiation of **3** in cyclohexane gave a mixture of alcohols which was difficult to analyze and whose composition appeared to change on standing. Treatment of the crude product with hexamethyldisilazane allowed the isolation of two silylated materials in a 2:1 ratio. The same two products were obtained by lithium aluminum hydride reduction of **3** and subsequent silylation. The major component retained the epoxide ring as demonstrated by its spectroscopic properties and by comparison with a sample obtained by silylation and epoxidation of 4-cyclooctenol.[20] However, the second silyl ether lacked ir and nmr characteristics of the epoxide function. The results from hydride reduction of **3** suggest initial formation of the expected *cis*- and *trans*-epoxy alcohols (**20** and **21**), followed by intramolecular displacement of the suitably disposed *trans*-hydroxyl of **21** on the transannular epoxide moiety which transforms it into a bridged bicyclic ether. Two

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[18] D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963).

[19] During the preparation of this work for publication, we learned of a related study of the photochemistry of **1** and **2** by Professor S. Moon whom we thank for a helpful exchange of information.

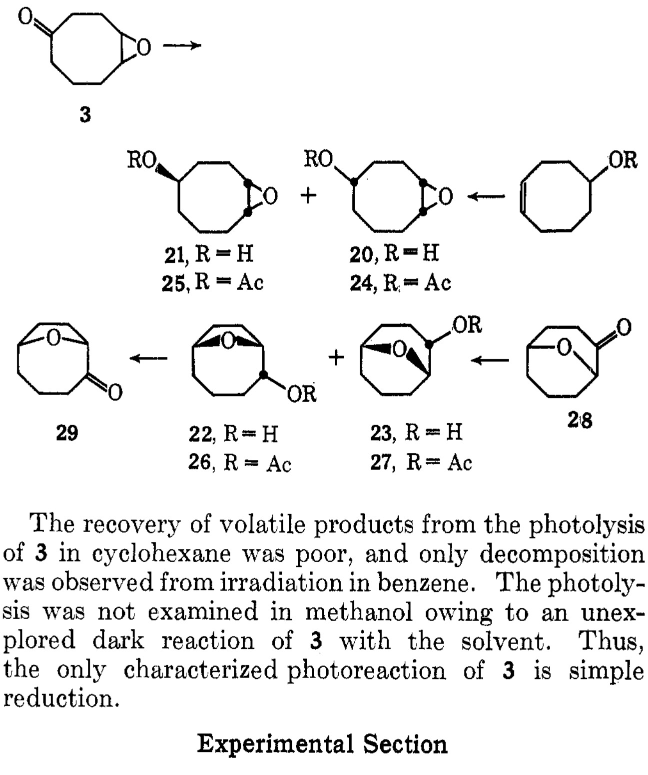
[20] This epoxidation apparently proceeds with high stereoselectivity presumably by attack of peracid cis to the silyl ether group.

different bicyclic ethers, **22** and **23**, are possible depending on the mode of transannular attack.[21]

Gas chromatographic studies utilizing acetate esters confirmed this hypothesis. Photolysis of **3** followed immediately by exposure to acetic anhydride–pyridine gave the same two peaks as obtained by epoxidation of 4-cyclooctenyl acetate. These are assigned as the *cis*- and *trans*-4,5-epoxycyclooctyl acetates (**24** and **25**). However, acetylation of the alcohol mixture obtained by epoxidation of 4-cyclooctenol gave only one of these peaks plus a second peak of the same retention time as an authentic unresolved mixture of bicyclic acetates **26** and **27**.[22] Treatment of the bicyclic acetate from either source with hydride followed by chromic acid oxidation gave a mixture of bicyclic ketones **28** and **29**.

The complicated set of interrelations described above establishes that the initial photoproducts are **20** and **21** and that under certain conditions **21** is further transformed to a mixture of the isomeric bicyclic ethers **22** and **23** (*e.g.*, under the conditions of silylation of the photoproduct, hydride reduction of **3**, and epoxidation of 4-cyclooctenol) (Scheme III).

SCHEME III



The recovery of volatile products from the photolysis of **3** in cyclohexane was poor, and only decomposition was observed from irradiation in benzene. The photolysis was not examined in methanol owing to an unexplored dark reaction of **3** with the solvent. Thus, the only characterized photoreaction of **3** is simple reduction.

Experimental Section

General.—Nmr spectra were obtained with Varian A-60 or HR-100 instruments (CCl_4) and infrared spectra with Perkin-Elmer 137 and 137G spectrophotometers (neat samples unless noted otherwise). Gas chromatography (gc) was performed on Aerograph A1200 (analytical) and A90-P3 (preparative) instruments. Analytical columns were 10 ft × $^1/_8$ in. 15% Carbowax 20M on 60–80 Chromosorb W and 10 ft × $^1/_8$ in. 15% diethylene glycol succinate on 60–80 Chromosorb W. Mass spectra were obtained at 70 eV on an AEI-MS 9 instrument. Anhydrous magnesium sulfate was used for all drying operations.

Preparative photolyses were carried out on 1% solutions with a 450-W medium-pressure Hanovia Type L mercury vapor lamp in an immersion-well apparatus using a Vycor filter. The solution was degassed by bubbling nitrogen through it prior to photolysis, and a positive nitrogen pressure was maintained during photolysis. The course of the reaction was monitored by analytical gc.

3-Cyclooctenyl Acetate.—A solution of 6.3 g of 3-cyclooctenol and 12 ml of acetic anhydride in 50 ml of pyridine was stirred at room temperature for 18 hr. The solution was poured into 10% hydrochloric acid and extracted four times with pentane. The pentane solution was washed with saturated aqueous sodium bicarbonate and water and dried, and the solvent was removed by evaporation on a steam bath. Distillation gave 6.2 g of 3-cyclooctenyl acetate: bp 108–110° (30 mm); ir 3.3, 5.76, 7.3, 8.1, and 9.7 μ; nmr δ 5.65 (m, 2, CH=CH), 4.8 (broad m, 1, CHOAc), and 2.6–1.1 (broad m, 13). A sharp singlet at 1.9 (CH_3CO) was superimposed over the methylene absorption.

Preparation of Bicyclo[6.1.0]nonan-3-yl Acetate.—A solution of 95 g of methylene iodide, 26 g of zinc-copper couple, and 100 mg of iodine in 250 ml of ether was stirred at reflux for 0.5 hr. The oil bath was removed, and 4.5 g of 3-cyclooctenyl acetate in 25 ml of ether was added dropwise. Heating was then resumed and the mixture stirred at reflux for 48 hr. The mixture was filtered through HyFlo Super Cel and the filtrate was washed with five 50-ml portions of 5% hydrochloric acid, then with saturated sodium bicarbonate solution, and water, and dried. Concentration, followed by distillation, gave 4.7 g (96%) of bicyclo[6.1.0]nonan-3-yl acetate: bp 110–115° (30 mm); ir 3.25, 3.33, 5.75, 7.3, 8.0, and 9.8 μ; nmr δ 4.8 (m, 1, CHOAc), 2.2–0.5 (m, 16, CH_2, CH_3, cyclopropyl H), and −0.2 (m, 1, cyclopropyl H). The presence of sharp singlets of nearly equal intensity at 1.85 and 1.90 indicates that the product is a mixture of isomers, even though it was homogeneous to gc.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.23; H, 10.00.

Bicyclo[6.1.0]nonan-3-ol.—To a solution of 3 g of potassium hydroxide in 50 ml of methanol was added 4.5 g of bicyclo[6.1.0]nonan-3-yl acetate, and the resulting mixture was stirred at reflux for 3 hr. The reaction mixture was poured into water and pentane, and the layers were separated. The organic layer was washed twice with water and dried. The solvent was removed on a flash evaporator, and the residue was distilled through a short-path distillation head to give 2.7 g (90%) of bicyclo[6.1.0]nonan-3-ol: bp 115–120° (20 nm); ir 3.0, 3.2, 3.3, and 9.6 μ; nmr δ 3.7 (m, 2, CHOH), 2.4–0.5 (m, 13, CH_2, cyclopropyl H), and −0.3 (m, 1, cyclopropyl H).

Bicyclo[6.1.0]nonan-3-one (1).—Five milliliters of 8 *N* chromic acid was added dropwise to a cooled, stirred solution of 2.9 g of bicyclo[6.1.0]nonan-3-ol in 50 ml of acetone. The mixture was stirred for 0.75 hr, poured into water, and extracted with four 50-ml portions of pentane. The organic solution was washed with water and dried, and the solvent was removed on a flash evaporator. Distillation gave 2.6 g (91%) of **1**: bp 98–105° (20 mm); uv max (hexane) 289 nm (ϵ 44) [lit.[7] 298 nm (ϵ 34)]; ir 3.24, 3.32, 5.88, and 11.7 μ; nmr δ 2.8–1.0 (m, 10), 0.7 (m, 3, cyclopropyl H), and −0.1 (m, 1, cyclopropyl H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.24; H, 9.95.

Photolysis of 1.—A solution of 0.9 g of **1** in 110 ml of methanol was photolyzed for 15 min. The solvent was removed by evaporation on a steam bath, and the residue was distilled (0.2 mm) to give 0.76 g of crude photoproduct. The products were isolated by preparative gc. The first product (27%) was identified as *trans*-5,8-nonadienal (**4**): ir 3.22, 3.33, 3.68, 5.80, 6.1, 10.1, 10.3, and 11.0 μ; nmr δ 9.5 (t, 1, J = 1 Hz, CHO), 6.1–4.7 (m, 5, CH=CH), and 3.0–1.3 (m, 8).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.09; H, 10.27.

The second product (18%) was methyl 8-nonenoate (**7**): ir (CCl_4) 3.24, 5.74, 6.1, 7.3, 8.4, 8.6, 10.1, and 11.0 μ; nmr δ 5.7 (m, 1, CH=CH_2), 4.9 (m, 2, CH=CH_2), 3.6 (s, 3, CH_3O), and 2.5–1.0 (m, 10).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.53; H, 10.71.

The third component (35%) was 2-allylcyclohexanone (**5**), identified by comparison with an authentic sample. The fourth product (10%) was identified as 3-vinylcycloheptanone (**6**) on spectroscopic grounds: ir (CCl_4) 3.24, 5.90, 6.1, 10.1, and 11.0 μ; nmr (100 MHz) δ 5.8 (m, 1, CH=CH_2), 5.0 (m, 2, CH_2=CH),

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[21] Related reactions are well precedented. See, for example, A. C. Cope, R. S. Bly, M. M. Martin, and R. C. Petterson, *J. Amer. Chem. Soc.*, **87**, 3111 (1965).

[22] S. Moon and L. Haynes, *J. Org. Chem.*, **31**, 3067 (1966); A. C. Cope, M. A. McKervey, and N. M. Weinshenker, *J. Amer. Chem. Soc.*, **89**, 2932 (1967).

and 2.6–1.2 (m, 11); mass spectrum *m/e* (rel intensity) 138 (30), 82 (32), 81 (100), 68 (46), 67 (67), 56 (61), and 55 (33).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.00; H, 10.16.

The fifth component (12%) was **1**.

Photolysis of **1** in cyclohexane or benzene required 45 min and gave **4** (14%), **5** (32%), **6** (14%), **1** (33%), and an unknown of short retention time (7%). No equilibration of **4**, **5**, or **6** with each other or starting material was observed when each of these products was irradiated in separate experiments.

Catalytic Hydrogenation of 7.—A solution of 25 mg of **7** in 5 ml of methanol was hydrogenated at atmospheric pressure with 5% palladium on carbon for 24 hr. The catalyst was removed by filtration and the filtrate was poured into water and pentane. The layers were separated and the aqueous layer was washed twice with pentane. The pentane extracts were washed with water and dried, and the solvent was removed by distillation to give 20 mg of methyl pelargonate, identical in all respects with an authentic sample.

Catalytic Hydrogenation of the Photoproducts of 1.—A solution of 450 mg of the crude photoproduct mixture from photolysis of **1** in benzene was hydrogenated in 15 ml of methanol at atmospheric pressure using 10% palladium on carbon as catalyst. After 24 hr, the catalyst was removed by filtration, and the filtrate was poured into water and extracted three times with pentane. The pentane extract was washed with water and dried, and the solvent was removed by distillation. Separation by preparative gc yielded *n*-nonanal, 2-*n*-propylcyclohexanone (each of which was identified by comparison of its ir spectrum with that of a known sample), and a material tentatively identified as 3-ethylcycloheptanone, ir 5.88 μ.

2-Allylcyclohexanone (5).—To 75 ml of a 0.8 *M* solution of commercial allylmagnesium bromide in ether was added dropwise 5 g of cyclohexene oxide in 25 ml of ether. The mixture was stirred at reflux for 12 hr and then poured into 75 ml of cold 5% hydrochloric acid and 50 ml of pentane. The layers were separated and the aqueous portion was washed with three 50-ml portions of pentane. The combined extracts were washed with water and dried, and the solvent was removed by distillation. The residue was distilled through a short-path distillation head to give 5.9 g (83%) of 2-allylcyclohexanol: bp 46–48° (0.8 mm); ir 3.0, 3.26, 6.1, 9.5, 9.7, 10.1, and 11.0 μ; nmr δ 6.1–4.7 (m, 3, $CH{=}CH_2$), 3.85 (s, 1, OH), 3.2 (m, 1, CHOH), and 2.6–0.9 (m, 11).

To a cooled, stirred solution of 4.2 g of 2-allylcyclohexanol in 50 ml of acetone was added dropwise 8 ml of 8 *N* chromic acid. The resulting mixture was stirred at room temperature for an additional 30 min, poured into water, and extracted with three 50-ml portions of pentane. The pentane solution was washed with water, dried, and concentrated. The residue was distilled to give 3.2 g (76%) of **5**: bp 82–86° (15 mm); ir 3.24, 5.84, 6.1, 10.1, and 11.0 μ; nmr δ 6.1–4.7 (m, 3, $CH{=}CH_2$) and 2.6–1.0 (m, 11).

4-Cyclooctenyl Acetate.—A solution of 10.5 g of 4-cyclooctenol and 15 ml of acetic anhydride in 40 ml of pyridine was stirred at room temperature for 18 hr. The reaction mixture was poured into 250 ml of 10% hydrochloric acid and 500 ml of pentane, and the layers were separated. The pentane was washed with two 50-ml portions of 10% hydrochloric acid, saturated aqueous sodium bicarbonate, and water and dried. The solvent was removed by distillation and the residue was distilled to give 12 g (86%) of 4-cyclooctenyl acetate: bp 110–113° (20 mm); ir, 3.3, 5.78, 7.3, and 8.1 μ; nmr δ 5.6 (m, 2, $CH{=}CH$), 4.7 (broad m, 1, CHOAc), 2.4–1.4 (m, 13). A sharp singlet (CH_3CO) at 1.9 was superimposed over the methylene multiplet.

Bicyclo[6.1.0]nonan-4-yl Acetate.—A solution of 75 g of methylene iodide, 20 g of zinc–copper couple, and 100 mg of iodine in 250 ml of ether was stirred at reflux for 30 min. The heating bath was removed, and 4.5 g of 4-cyclooctenyl acetate in 25 ml of ether was added dropwise. The resulting mixture was stirred at reflux for 48 hr. The mixture was filtered through HyFlo Super Cel and the filtrate was washed with five 50-ml portions of 5% HCl, then with saturated aqueous sodium bicarbonate, and water and dried. The solvent was removed by flash evaporation and the residue was distilled to give 4.7 g (86%) of bicyclo[6.1.0]nonan-4-yl acetate: bp 120–125° (2 mm); ir 3.2, 3.3, 5.76, 7.3, and 8.1 μ; nmr δ 4.9 and 4.7 (m, 1, CHO), 2.4–0.3 (m, 16), and −0.3 (m, 1, cyclopropyl H). A sharp singlet (CH_3CO) at 1.9 was superimposed upon the broad methylene absorption.

Bicyclo[6.1.0]nonan-4-ol. A.—To a stirred, cooled slurry of 20 g of mercuric acetate in 120 ml of 50% aqueous tetrahydrofuran was added dropwise 7.0 g of bicyclo[6.1.0]non-4-ene. The yellow color disappeared before addition was complete (*ca.* 5 min), and the solution was stirred at room temperature for 45 min. The reaction mixture was again cooled in an ice bath, and 60 ml of 3 *N* sodium hydroxide and 60 ml of 0.5 *M* sodium borohydride in 3 *N* sodium hydroxide were added slowly. The solution was saturated with sodium chloride and the layers were separated. The aqueous solution was washed twice with tetrahydrofuran, the combined tetrahydrofuran extracts were washed with water and dried, and the solvent was removed by distillation. The residue was distilled through a short-path distillation head to give 6.5 g (81%) of bicyclo[6.1.0]nonan-4-ol: bp 60–63° (1 mm); ir 3.0, 3.26, 3.34, 9.6, 9.7, 10.0, 10.6, and 11.9 μ; nmr (100 MHz) δ 4.0 and 3.5 (two complex multiplets in a ratio of 6:4, together integrating for 1 hydrogen, CHOH), 2.5 (s, 1, OH), 2.3–0.5 (m, 13, CH_2, cyclopropyl H), and −0.7 (m, 1, cyclopropyl H). The sample was homogeneous on a variety of gc columns.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.89; H, 11.46.

B.—To a solution of 3.2 g of potassium hydroxide in 55 ml of methanol was added 4.2 g of bicyclo[6.1.0]nonan-4-yl acetate, and the resulting solution was stirred at reflux for 2.5 hr. The reaction mixture was poured into water and pentane, and the layers were separated. The pentane layer was washed three times with water and dried, and the solvent was removed by flash evaporation. Distillation gave 2.5 g (77%) of bicyclo[6.1.0]-nonan-4-ol.

Trimethylsilylation of Bicyclo[6.1.0]nonan-4-ol.—A mixture of 227 mg of the product obtained in the previous experiment and 550 mg of hexamethyldisilazane was stirred at 85–90° for 12 hr. Gc analysis showed two products of shorter retention time than the starting alcohol in a ratio of 56:44. Preparative gc gave two products which are assigned as the trimethylsilyl ethers of *cis*- and *trans*-bicyclo[6.1.0]nonan-4-ol (**13** and **14**). The 56% isomer shows absorptions in the nmr at δ 3.9 (m, 1, CHO), 2.2–0.3 (m, 13), 0.0 (s, 9, CH_3Si), and −0.3 (m, 1, cyclopropyl H). The 44% isomer exhibits an nmr identical with that of the first component, except that the downfield multiplet is shifted to 3.3.

Bicyclo[6.1.0]nonan-4-one (2).—To a cooled, stirred solution of 6.2 g of bicyclo[6.1.0]nonan-4-ol in 60 ml of acetone was added dropwise 12 ml of 8 *N* chromic acid, and the solution was stirred for an additional 15 min. The reaction mixture was poured into 40 ml of water and extracted with five 50-ml portions of pentane. The combined pentane extracts were washed with water and dried and the solvent was removed by flash evaporation. Distillation of the residue gave 4.0 g (66%) of **2**: bp 99–101° (15 mm); uv max (hexane) 287 nm (ϵ 15); ir 3.25, 3.33, and 5.86 μ; nmr δ 2.3 (m, 4, CH_2CO), 2.1–1.3 (m, 6, CH_2), 0.6 (m, 3, cyclopropyl H), and −0.2 (m, 1, cyclopropyl H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.34; H, 10.24.

Photolysis of 2. A. Methanol.—A solution of 1.0 g of **2** in 110 ml of methanol was photolyzed for 1 hr. The solvent was removed by evaporation on a steam bath and the residue distilled (0.1 mm) to give 0.8 g of crude photoproduct. The products were isolated by preparative gc (20 ft × 0.25 in. 20% UCON 2000 Polar, 160–180°). The first component was ethylene glycol. The second product (20%) was identified as **15** on the basis of its spectral properties: ir 3.24, 3.33, 3.67, 5.80, 6.1, 10.1, and 11.0 μ; nmr (100 MHz) δ 9.57 (t, 1, J = 1 Hz, CHO), 5.8 (m, 1, $CH{=}CH_2$), 5.0 (m, 2, $CH{=}CH_2$), 2.45 (triplet of t, 2, J = 7, 1 Hz, CH_2CHO), 2.0 (m, 2, $CH_2{=}CHCH_2$), 1.6 (m, 2, CH_2), 0.75 (m, 3, cyclopropyl H), and −0.2 (m, 1, cyclopropyl H). Double irradiation experiments confirmed this structure, since irradiation of the methylene multiplet at 2.0 effected a simplification of the vinyl resonance, thereby demonstrating that the vinyl group was part of a side chain terminated by an allyl group. Irradiation of either the aldehyde resonance at 9.57 or the methylene absorption at 2.45 clearly demonstrated the mutual coupling of these two groups.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.10; H, 10.32.

The third component (3%) is tentatively identified as 4-(*cis*-2-vinylcyclopropyl)butanal (**16**): ir 3.25, 3.33, 5.80, 6.1, 10.1, and 11.0 μ; the nmr shows a spectrum nearly identical with that of **15** except that the vinyl resonance is somewhat simpler.

The fourth product (25%) was identified as methyl 3-(*cis*-2-*n*-propylcyclopropyl)propanoate (**17**): ir 3.25, 3.33, 5.74, 7.3, and 8.6 μ; nmr δ 3.61 (s, 3, CH_3O), 2.3 (m, 2, CH_2CO), 2.0–0.5 (m, 14), and −0.2 (m, 1, cyclopropyl H). In addition, a multiplet typical of an aliphatic methyl was observed at 1.0. This product was homogeneous to a variety of gc columns and was identical with a sample prepared from aldehyde **15**.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.46; H, 10.71.

The fifth component (1%) was not isolated in sufficient quantity to identify it. The sixth component (36%) was starting ketone. The seventh component (15%) was identified as a mixture of the bicyclo[6.1.0]nonan-4-ols (**13** and **14**) by comparison with authentic material.

B. Cyclohexane.—A solution of 1.0 g of **2** was photolyzed for 45 min; gc analysis showed two major products in addition to starting material. Concentration and distillation gave 0.8 g of crude product. The first product was identified as bicyclohexyl by comparison with authentic material. The other two components were identified as starting material (33%) and the isomeric bicyclo[6.1.0]nonan-4-ols (67%).

C. Isopropyl Alcohol.—Photolysis of a 50-mg sample of **2** in 5 ml of isopropyl alcohol led to a mixture of starting material (30%) and the isomeric bicyclo[6.1.0]nonan-4-ols (3:1) (70%).

D. Benzene.—Photolysis of a 10-mg sample of **2** in 1 ml of benzene in a Rayonet photochemical reactor with 3100-Å lamps led to a very slow decomposition of starting material with no discrete product formation.

4,5-Epoxycyclooctanone (3).—A solution of 17 ml of 40% peracetic acid was added dropwise to a cooled, stirred mixture of 5.4 g of 4-cyclooctenone, 29 g of anhydrous sodium carbonate, and 100 ml of methylene chloride. The reaction was stirred at room temperature for 48 hr, and the solid salts were removed by suction filtration and washed thoroughly with additional methylene chloride. The filtrate was washed with water, dried, and concentrated. The pasty residue was purified by sublimation to give 5.0 g (82%) of **3**. Low-temperature recrystallization from ether and sublimation gave a pure sample: mp 85–86°; uv max (hexane) 288 nm (ε 13); ir (CCl_4) 5.86, 9.9, 10.4, 11.0, and 11.6 μ; nmr very sharp, complex absorption pattern from δ 2.9 to 1.5.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.54; H, 8.88.

Photolysis of 3.—A solution of 1.1 g of **3** in 110 ml of cyclohexane was irradiated for 1.25 hr. The solvent was removed to give 0.7 g of crude product: ir 3.0, 5.85, and 9.6 μ. The crude product was stirred at 90° in excess hexamethyldisilazane for 18 hr. Three components in addition to **3** (32%) were isolated from the product thus obtained by preparative gc. The first product was bicyclohexyl. The second product (23%) displayed ir 3.5, 8.0, 9.4, 11.4, and 11.9 μ; nmr (100 MHz), δ 4.4–3.5 (m, 3, CHO), 2.3–1.1 (m, 10, CH_2), and 0.1 (s, 9, CH_3Si).

Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.66; H, 10.34. Found: C, 61.72; H, 10.44.

The third product (45%) was 4,5-epoxycyclooctyl trimethylsilyl ether: ir 3.5, 8.0, 9.1, 9.6, 10.9, 11.1, 11.4, 11.9, and 13.4 μ; nmr (100 MHz) δ 3.9 (m, 1, CHOSi), 2.75 (m, 2, epoxide H), 2.2–1.0 (m, 10, CH_2), and 0.05 (s, 9, CH_3Si).

Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.66; H, 10.34. Found: C, 61.58; H, 10.29.

A solution of 46 mg of **3** in 4.6 ml of cyclohexane in a Pyrex test tube was degassed and irradiated in a Rayonet photochemical reactor with 3000-Å bulbs for 6 hr. The solvent was removed under reduced pressure, the residue was dissolved in 1 ml of dry pyridine, and 0.4 ml of acetic anhydride was added. After standing for 17 hr at room temperature, the mixture was diluted with water and extracted with pentane. The pentane extract was washed with 1 *N* hydrochloric acid and saturated sodium carbonate solution and dried, and the solvent was removed. Gc assay of the residue displayed two peaks in a 4:1 ratio. These peaks were shown to have the same gc elution times as *cis*- and *trans*-4,5-epoxycyclooctyl acetates (**24** and **25**) prepared by peracid oxidation of 4-cyclooctenyl acetate.

When the photolysis was repeated with an internal standard, it was observed that more than half of the **3** was converted to nonvolatile products.

Reaction of 3.—To a cooled, stirred slurry of 200 mg of lithium aluminum hydride in 50 ml of anhydrous ether was added dropwise 1.0 g of **3** in 10 ml of ether. The resulting mixture was stirred at 0° for 3 hr, and hydrolysis was effected by addition of 2 ml of water. Magnesium sulfate was added, and the solid material was removed by suction filtration and washed with additional solvent. The filtrate was concentrated to give 0.9 g of a viscous liquid which was stirred at 85° with 6 ml of hexamethyldisilazane for 30 hr. Gc analysis showed two products in a ratio of 1:8 which were collected by preparative gc and were found to be identical with the silyl ethers obtained from the photolysis of **3**.

4,5-Epoxycyclooctyl Trimethylsilyl Ether.—A mixture of 0.75 g of 4-cyclooctenol in 3 ml of hexamethyldisilazane was stirred at 85° for 48 hr. The resulting trimethylsilyl ether (0.5 g) was collected by preparative gc and added to 25 ml of ice-cold methylene chloride containing 10 g of anhydrous sodium carbonate, and a methylene chloride solution of acetic acid–free peracetic acid[23] obtained from 1 ml of 40% peracetic acid was added. The resulting solution was stirred for 18 hr and then suction filtered. The solid filter cake was washed with methylene chloride, and the filtrate was concentrated to give a crude product from which the trimethylsilyl ether of **20** was collected by preparative gc. This material was identical with that obtained from the reactions described above except for minor differences in the nmr attributable to small amounts of the epimeric ether.

***cis*- and *trans*-4,5-Epoxycyclooctyl Acetate (24 and 25).**[24]—To a solution of 0.78 g of 4-cyclooctenyl acetate in 50 ml of methylene chloride at 0° was added 0.79 g of *m*-chloroperoxybenzoic acid in small portions with swirling. After standing for 18 hr, the solution was washed with saturated sodium carbonate solution and dried. Removal of the solvent gave a colorless oil: ir 5.77, 8.0, 9.7, and 9.8 μ. Gc analysis showed a 3:1 ratio of **24** to **25**.

Epoxidation of 4-Cyclooctenol.—To an ice-cold solution of 1.0 g of 4-cyclooctenol in 50 ml of methylene chloride was added 1.46 g of *m*-chloroperoxybenzoic acid in small portions with swirling. After standing for 13 hr at room temperature, the solution was washed with two 20-ml portions of saturated sodium carbonate solution and dried, and the solvent was removed to give 1.28 g of colorless oil.

To a solution of 0.5 g of the above mixture in 5 ml of dry pyridine was added 1.88 ml of acetic anhydride. The solution was allowed to stand at room temperature for 20 hr. After being cooled to 0°, water was added slowly to hydrolyze the excess acetic anhydride before dilution to 50 ml. The resulting solution was extracted with pentane. The pentane solution was washed with 1 *N* hydrochloric acid and dried. Removal of the solvent gave a colorless oil: ir 5.77, 8.0, 9.4, 9.6, 9.7, and 9.8 μ. Gc assay showed a 3:2 ratio of two peaks. The smaller of these corresponds in gc elution time to the peak assigned as **24**. The larger peak corresponds in retention time to a gc inseparable mixture of *endo*-9-oxabicyclo[4.2.1]non-2-yl acetate (**26**) and *endo*-9-oxabicyclo[3.1.1]non-2-yl acetate (**27**) obtained by treatment of 4-cyclooctenol with lead tetraacetate.[22]

To a stirred, ice-cold solution of 0.5 g of the original epoxidation mixture in 10 ml of acetone was added dropwise 8 *N* chromic acid solution until the reagent color persisted. Excess oxidizing agent was destroyed by the addition of isopropyl alcohol. The mixture was diluted to 50 ml with water and stirred until the chromium salts dissolved. The solution was extracted with pentane, and the pentane solution was dried. The solvent was removed to give a colorless oil. Gc analysis showed two peaks, one of which corresponded to **3**. The mixture was separated by gc, and the second peak was shown by nmr analysis to be a 1:2 mixture of **28** and **29** by comparison of the ir and nmr spectra to those of pure **29**[25] and to a 1:1 mixture of the two ketones obtained by lithium aluminum hydride reduction of the acetates from treatment of 4-cyclooctenol with lead tetraacetate followed by chromic acid oxidation.

Registry No.—**1**, 28399-86-2; **2**, 22562-46-5; **3**, 28399-88-4; **4**, 28399-92-0; **5**, 94-66-6; **6**, 28399-94-2; **7**, 20731-23-1; **15**, 28405-41-6; **17**, 28405-54-1; 3-cyclooctenyl acetate, 28339-89-5; bicyclo[6.1.0]nonan-3-yl acetate, 28399-90-8; bicyclo[6.1.0]nonan-3-ol, 28399-91-9; 2-allylcyclohexanol, 21895-83-0; 4-cyclooctenyl acetate, 22445-58-5; bicyclo[6.1.0]nonan-4-yl acetate, 28405-39-2; bicyclo[6.1.0]nonan-4-ol, 28405-40-5; 4,5-epoxycyclooctyl trimethyl silyl ether, 28405-53-0.

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