Tetrahedron Vol. 48, No. 8, pp. 1427-1448, 1992
Printed in Great Britain

0040-4020/92 $3.00+.00

Allene Epoxidation. Highly Functionalized Tetrahydrofurans and Tetrahydropyrans from the Oxidative Cyclization of Allenic Alcohols.

Jack K. Crandall,* David J. Batal, Feng Lin, Thierry Reix, Gregory S. Nadol, and Raymond A. Ng
Department of Chemistry, Indiana University, Bloomington, Indiana 47405

(*Received in USA* 30 *December* 1991)

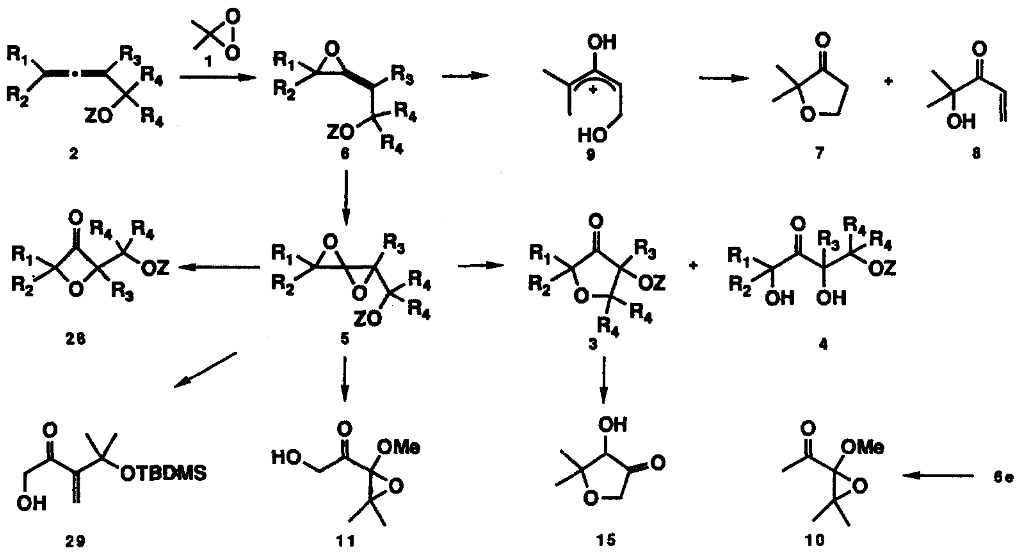
Abstract: *The dimethyldioxirane oxidation of various allenic alcohols yields highly functionalized tetrahydrofuran and tetrahydropyran derivatives via intramolecular nucleophilic addition of the hydroxy group to an intermediate allene diepoxide.*

In an extention of our studies on the epoxidation chemistry of allenes,[1] we have recently shown that the use of dimethyldioxirane (**1**) as an oxidant[2] provides for easy access to the diepoxides of simple allenes (1,4-dioxaspiro[2.2]pentanes or spirodioxides), which undergo facile substitution reactions with a range of nucleophilic species with classical S_N2 selectivity.[3] In this contribution we detail our studies of allenic alcohols capable of intramolecular nucleophilic additions subsequent to epoxidation of the allene unit. These transformations lead to a variety of highly functionalized oxygen heterocycles,[4,5] which potentially are useful synthetic intermediates. Earlier work by Bertrand and collaborators[6] showed that Payne and peracid oxidations of allenyl alcohols provided interesting cyclic products derived from mono-epoxidation of the allene function. At about this time, Conover[7] first found that peracids could also give products which appeared to involve the corresponding diepoxides as intermediates. The use of oxaziridines[8] as oxidants for allenyl alcohols gave preliminary results similar to those with peracids. However, these studies were abandoned with the timely publication by Murray[9] of a method for the preparation of acetone solutions of **1**. This reagent provides a simple protocol for epoxidation and other oxidation processes under neutral, non-nucleophilic conditions.

RESULTS

In general, the oxidation reactions were simply performed by addition of the allenic alcohols to three or more equivalents of **1** in acetone solution. The disappearance of starting material, as indicated by TLC monitoring, was followed by removal of solvent and excess oxidant, and spectroscopic examination and/or isolation by chromatographic methods. Results are summarized below according to the relationship of the allene and alcohol functions in the starting materials.

α-Allenyl alcohols. The types of products derived from these starting materials are quite dependent on the nature of the substitution pattern of the allene unit. Thus, the trisubstituted allenic alcohol **2a** gave furanone **3a** as the major product (55% yield), accompanied by 10% of the acyclic triol **4a**. No intermediate was ever observed in this reaction, but spirodioxide **5a** is a likely reactive precursor of **3a** and **4a**, which are formed by nucleophilic cyclization and hydration, respectively. The latter is effected by the traces of water which are always present in the oxidant solutions. Interestingly, the purposeful addition of water did not increase the amount of **4a** produced. Detectable quantities of products formed by trapping of an intermediate allene oxide **6a** were not observed under these conditions, suggesting that a second oxidation occurs more rapidly than cyclization or hydration of **6a**. However, when the oxidation of **2a** was performed in the presence of *p*-toluenesulfonic acid (TsOH) and diluted with CH_2Cl_2 as a cosolvent, the major product was the less highly oxidized furanone **7**, accompanied by small amounts of **3a** and enone **8**. This result is attributable to



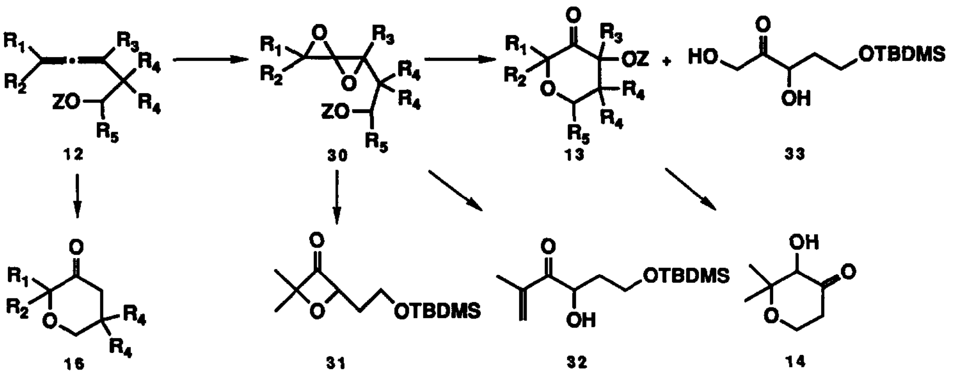
	R_1	R_2	R_3	R_4	Z		R_1	R_2	R_3	R_4	Z		R_1	R_2	R_3	R_4	Z
a	Me	Me	H	H	H	d	*n*Bu	H	H	Me	H	g	H	H	Me	H	TBDMS
b	H	H	Me	H	H	e	Me	Me	H	H	TBDMS	h	H	H	*n*Bu	H	TBDMS
c	H	H	OMe	Me	H	f	H	H	H	H	TBDMS	i	*n*Bu	H	H	Me	TBDMS

trapping of **6a** by protonation and irreversible ring-opening to give hydroxyallyl cation **9**, which proceeds on to **7** by cyclization and tautomerization. Interestingly, the disubstituted terminal allenic alcohol **2b** gave only the trapping of **6a** by protonation and irreversible ring-opening to give hydroxyallyl cation **9**, which proceeds on to hydration product **4b** upon the usual treatment with an acetone solution of **1**.

On the other hand, the methoxy-substituted allenic alcohol **2c** gave a mixture of cyclic products derived from both the intermediate allene oxide **6c** and the spirodioxide **5c**. In this case, ring-closure occurs by intramolecular attack of the hydroxyl at the methoxy-bearing carbon center, so as to generate epoxides **10** and **11** in a 1:3 ratio. The latter was converted to its *tert*-butyldimethylsilyl (TBDMS) ether to facilitate isolation. Thus, the methoxy group provoked competitive cyclization at the allene oxide stage, even in the presence of solid potassium carbonate to scavenge acid. This substituent also reversed the regiochemistry of these cyclizations, so that nucleophilic attack occurred at the methoxy-bearing carbon even at the cost of forming an epoxide ring.

The 1,3-disubstituted allenic alcohol **2d** was oxidized by **1** to a 1.2:1 mixture of *cis* and *trans* furanone **3d**. The lack of significant stereochemical control in this conversion is notable.

β-Allenyl alcohols. These alcohols usually provide cyclic materials efficiently, although the tendency for isomerization of the initial products is a complicating feature. The trisubstituted allenic alcohol **12a** was oxidatively cyclized by **1** to give pyranone **13a** in 92% yield. This compound underwent a facile ketol rearrangement to isomeric pyranone **14**, a process that could be performed preparatively by stirring an ether-chloroform solution of **13a** with silica gel for several hours. This conversion proceeds essentially to completion, indicating the greater stability of the arrangement of functionality in **14**. (The furanone **3a** appears to undergo a similar transposition to **15**, but in this case a 1:1 mixture of isomeric ketols is formed.) Running the oxidation of **12a** by adding the solution of **1** to **12a** in CH_2Cl_2 solution containing TsOH gave the simple pyranone **16a** as the major product, plus 10% of **13a**, indicating that cyclization at the mono-epoxidation stage could once again



	R_1	R_2	R_3	R_4	R_5	Z		R_1	R_2	R_3	R_4	R_5	Z		R_1	R_2	R_3	R_4	R_5	Z
a	Me	Me	H	H	H	H	e	*n*Pr	H	H	H	H	H	i	*n*Pr	H	H	Me	H	TBDMS
b	H	H	H	Me	H	H	f	Me	Me	H	H	Me	H	j	Me	Me	H	H	H	TBDMS
c	Me	Me	Me	H	H	H	g	Me	Me	H	Me	H	H	k	*n*Pr	H	H	H	H	TBDMS
d	*n*Pr	H	H	Me	H	H	h	H	H	H	Me	H	TBDMS	l	H	H	H	H	H	TBDMS

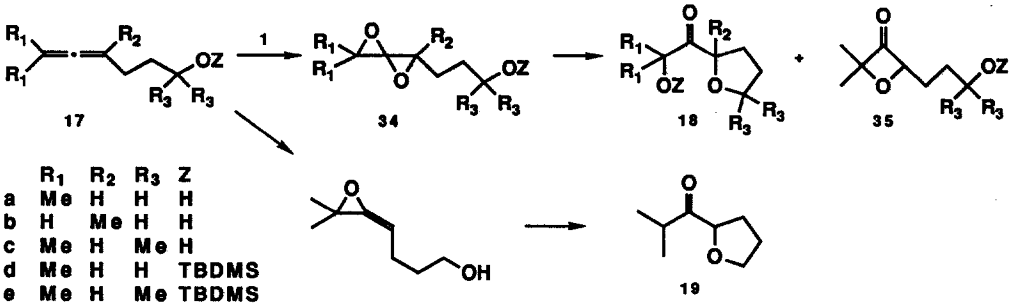
be forced by the presence of strong acid.

Interestingly, the monosubstituted allene **12b** was also cleanly converted to cyclic product **13b** by **1** under the usual oxidation conditions, in clear contrast to the situation with the terminally unsubstituted α-allenyl alcohol **2b**. Tetrasubstituted allene **12c** was likewise efficiently transformed to pyranone **13c**.

The disubstituted allenic alcohol **12d** provides an example where diastereomeric pyranones are possible. In this case, the usual oxidation gave a 2.5:1 mixture of *trans* **13d** and *cis* **13d**, which was converted to a mixture of the corresponding TBDMS ethers **13i** by TBDMS triflate. Stereochemical assignments in both instances are based on a characteristic small cross-carbonyl coupling constant (J = 1 Hz) of the α protons in the NMR of the *cis* isomers only.[10] A similar conversion of alcohol **12e** gave a 1.5:1 mixture of diastereomeric *trans* and *cis* pyranones **13e**. The secondary β-allenyl alcohol **12f** was also oxidatively cyclized without significant stereoselectivity to give a 1.3:1 ratio of *trans* to *cis* **13f**.

Experimentation with an *in situ* oxidation procedure, which might be more conveniently applied to larger scale reactions, was conducted using allenic alcohol **12g**. The usual oxidation of **12g** with a preformed solution of **1** in acetone yielded crystalline pyranone **13g** cleanly in 72% yield. Reactions incorporating **12g** into a biphasic mixture (water and benzene or methylene chloride) containing Oxone, sodium bicarbonate and acetone gave in moderate yield a mixture (*ca* 3:1 to 1:1) of **13g** and pyranone **16g**, derived from competitive cyclization of an allene oxide intermediate. A phase-transfer catalysis was initially used in accord with the literature for such oxidations,[11] but this was subsequently shown to be superfluous, as might be expected. A rather large excess of Oxone was required to consume all of the starting material in these procedures. A reaction omitting the buffering bicarbonate resulted in **16g** as the major product, in accord with the expectation of acid-catalysis in the cyclization leading to this material. Finally, the extra oxidizing power of trifluromethylmethyldioxirane[12] was utilized in a gram-scale oxidation of **12g** in water-methylene chloride containing several mL of trifluoroacetone, which led to a 66% yield of a 2:1 mixture of **13g** and **16g**. This procedure appears to be a promising development for larger-scale reactions which is currently being studied.

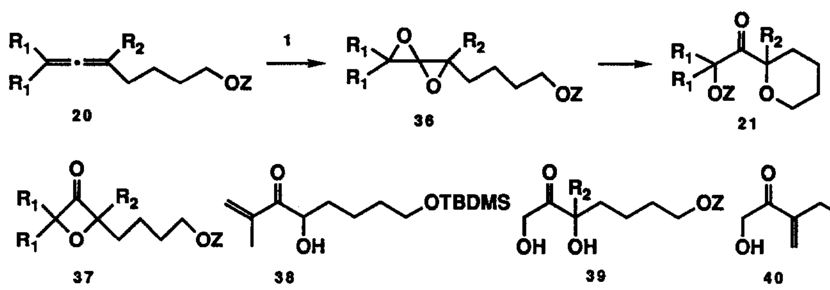
γ-Allenyl alcohols. Alcohols **17** were good substrates for oxidative cyclizations using solutions of



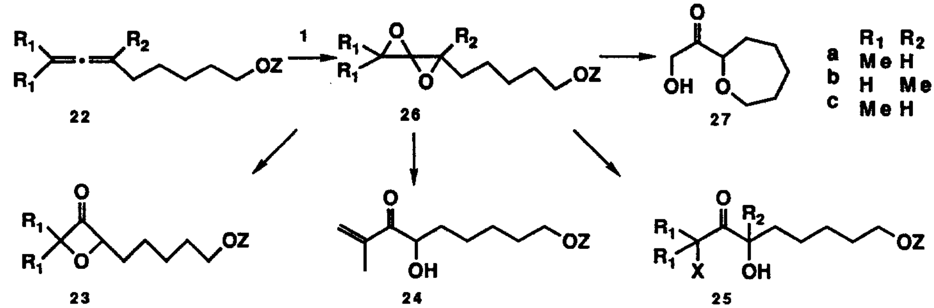
	R_1	R_2	R_3	Z
a	Me	H	H	H
b	H	Me	H	H
c	Me	H	Me	H
d	Me	H	H	TBDMS
e	Me	H	Me	TBDMS

1. Not unexpectedly, the regiochemistry of these cyclizations was reversed so as to give the tetrahydrofurans **18** generated by intramolecular attack of the hydroxyl at the proximate carbon of the spirodioxide unit. Thus, trisubstituted allenic alcohol **17a** gave **18a** in good yield. As before, an oxidation in the presence of TsOH resulted in the predominant formation of the less highly oxidized product **19** via cyclization after the first epoxidation step. Disubstituted allenic alcohol **17b** was cyclized to **18b** by **1**, albeit in lower yield (owing no doubt to competing hydrolysis of the spirodioxide intermediate). Tertiary allenic alcohol **17c** also gave the corresponding tetrahydrofuranyl ketone **18c** cleanly.

δ-Allenyl alcohols. As anticipated, these allenes were converted to the corresponding tetrahydropyranyl ketones without complication. Thus, the variously substituted alcohols **20a**, **20b**, and **20c** were oxidatively cyclized to **21a** (75%), **21b** (65%), and **21c** (55%), respectively.



	R_1	R_2	Z
a	Me	H	H
b	H	Me	H
c	H	H	H
d	Me	H	TBDMS
e	H	H	TBDMS
f	H	Me	TBDMS



	R_1	R_2	Z
a	Me	H	H
b	H	Me	H
c	Me	H	TBDMS

ε-Allenyl alcohols. The trisubstituted allenic alcohol **22a** initially gave only a mixture of rearrangement (**23**, **24a**) and hydration (**25a**, X = OH) products. However, the inclusion of solid K_2CO_3 into the reaction permitted the corresponding spirodioxide **26a** to be isolated. This is the first time such an intermediate has been observed from an allenic alcohol. Gratifyingly, heating **26a** in $CDCl_3$ in the presence of K_2CO_3 promoted a slow, but efficient cyclization to the oxepanyl ketone **27**.

Terminal allene **22b**, however, gave only the hydration product **25b** (X = OH) under all experimental conditions examined. The inclusion of potassium acetate into an oxidation of **22b** did permit the regioselective trapping of the intermediate spirodioxide to give **25b** (X = OAc).

Allenic silyl ethers. Conversion of allenic alcohols into their TBDMS ethers prior to oxidation with **1** generally allowed for isolation of the corresponding spirodioxides, although this was difficult for the monosubstituted allenes, where hydration of the spirodioxide was quite facile. The stereoselectivities of these transformations to spirodioxides largely parallel those observed for nonfunctionalized allenes.[3] In some instances, these silyloxy-substituted spirodioxides undergo cyclization upon heating in a manner akin to that postulated for the analogous alcohols, so as to provide silyl-protected products directly. In other cases, heating the spirodioxides provoked the typical rearrangements of the spirodioxide moiety to give oxetanones and conjugated enones.[3] The relative disposition of the two functions and the degree of substitution of the spirodioxide unit both appear to have a role in determining the course of these thermal isomerizations.

The cyclization of silyl ethers was first observed with the trisubstituted α-allenyl TBDMS ether **2e**, which gave furanone **3e** upon heating of the isolated spirodioxide **5e** for 2.5 hours at 65°C in $CDCl_3$ containing solid sodium bicarbonate. However, this was the only example of a silyl ether of an α-allenyl alcohol that cyclized predominantly in this fashion. The parent silyl ether **2f** gave hydration product **4f** directly upon oxidation with **1**; intermediate spirodioxide **5f** was not observed with this monosubstituted allene. The disubstituted, terminal spirodioxide **5g** was obtained from allene **2g** as a 2:1 mixture of *anti* and *syn* isomers, but heating **5g** in CCl_4 gave a complex mixture whose IR and NMR spectra indicated the presence of oxetanone **28g** and conjugated enone **29** as important components. The related allene **2h** with a larger butyl group at C_2 also provided a diastereomeric mixture of spirodioxides **5h** (1.1:1 ratio), but thermolysis gave an even more intractable mixture Interestingly, the sterically congested 1,3-disubstituted spirodioxide **5i**, formed as a 2:1 mixture of diastereomers by oxidation of **2i**, was resistant to prolonged heating in CCl_4.

The TBDMS ethers of β-allenic alcohols presented a different reactivity profile. Thus, the monosubstituted allenyl ether **12h** produced pyranone **13h** upon oxidation with **1** under the usual conditions, presumably by spontaneous cyclization of reactive spirodioxide **30h**. The related disubstituted allene **12i** gave an isolated 2.2:1 diastereomeric mixture of spirodioxides of structure **30i**, assigned as the *anti, anti* and *anti, syn* isomers.[3] Interestingly, this highly substituted spirodioxide resisted conversion on prolonged heating in refluxing benzene. The trisubstituted allene **12j** also generated isolable spirodioxide **30j** upon reaction with **1**. In this case, thermolysis in refluxing toluene converted **30j** to a 5:1 mixture of oxetanone **31** and conjugated enone **32**. The oxidation of **12k** followed by heating in refluxing $CHCl_3$ gave cyclic product **13k** as a mixture of isomers, but this conversion was not clean.

Oxidation of the monosubstituted allene ***12l*** under the usual conditions resulted in hydrolysis of the spirodioxide ***30l*** to diol **33** as the major process, but performing this reaction in the presence of anhydrous $MgSO_4$ permitted the observation of a 3.4:1 mixture of diasteriomers of ***30l*** by NMR. Heating ***30l*** in CCl_4 containing solid $MgSO_4$ resulted in cyclization to pyranone ***13l*** in modest yield (46%).

The primary γ-allenyl silyl ether **17d** gave a 9:1 mixture of *anti* and *syn* spirodioxides **34d**, but oxetanone **35d** was the major product formed upon heating. The related tertiary silyl ether **17e** behaved similarly, giving the same 9:1 ratio of spirodioxides **34e**, which generated oxetanone **35e** thermally.

The trisubstituted δ-allenyl TBDMS ether **20d** also yielded the typical 9:1 mixture of spirodioxides **36d**. A mixture of oxetanone **37d** and enone **38** was formed upon thermolysis of **36d**. Oxidation of the parent α-allenyl derivative **20e** was difficult to control; not only was hydrolysis a problem, but the low reactivity of the unsubstituted allene resulted in incomplete conversion. Thus, reaction of **20e** with a cold solution of **1** in the presence of $NaHCO_3$ gave a mixture of starting material and hydrolysis product **39e**. However, excess anhydrous $MgSO_4$ permitted the isolation of cyclized tetrahydropyran **21e** as the major product, along with some **39e**. Unfortunately, this transformation was difficult to reproduce; the source of the drying agent and the specific history of the oxidant were both important considerations here. The terminal disubstituted allene **20f** was oxidized to a 2:1 mixture of spirodioxide **36f**. However, the major products found upon refluxing **36f** in CCl_4 were the hydrolysis product **39f**, rearranged oxetanone **37f** and enone **40**.

Finally, the ε-allenyl ether **22c** behaved like its lower homologs. Thus, the 9:1 mixture of spirodioxides **26c** derived from **22c** gave mainly oxetanone **24c** upon thermolysis.

DISCUSSION

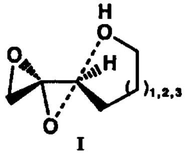
The oxidative cyclization of allenic alcohols has been shown to be a rather versatile reaction for the formation of highly functionalized oxygen heterocycles. Ring closure ordinarily occurs only after sequential epoxidation of the allene to a spirodioxide unit, but subsequent intramolecular addition of the neighboring hydroxyl occurs so rapidly that the spirodioxide species is not isolated. The only exception observed in this work involves spirodioxide **26**, where cyclization is retarded by the separation of the interacting functions by a five-carbon chain. Although the initially formed allene oxides are highly reactive intermediates, cyclization is generally slow with respect to the second epoxidation. Consequently, intramolecular trapping at this stage was important only with the activated methoxy-substituted allene **2c**, in the presence of strong acid, and during the *in situ* oxidations where the instantaneous concentration of oxidant **1** was low. The regiochemistry of the intramolecular nucleophilic reaction is controlled by the length of the carbon tether so as to give favorable five- and six-membered heterocycles by either *endo-* or *exo*-cyclization modes as required.[13] Once again methoxy-substituted allene **2c** provides a glaring, but understandable exception; a three-membered ring is generated by *exo* cyclization at both allene oxide and spirodioxide stages.

Cyclizations are thought to proceed by nucleophilic attack on an intact spirodioxide unit with the usual inversion of configuration at the reactive carbon site.[3] Further unraveling of the hemiacetal moiety thus formed, in a manner similar to the reaction of simple spirodioxides with external nucleophiles, leads to the heterocyclic α-hydroxyketones observed as stable products. In order for this to happen, the hydroxyl-bearing side-chain must be able to approach the reacting C-O bond from the backside in a reasonably colinear direction. This poses no problem for *exo* cyclization where bond rotation can provide a suitable transition state of type **I**, regardless of the stereochemistry of the spirodioxide unit. Interestingly, alkyl substitution at the spirodioxide carbon suffering attack, or at the more remote center, does not greatly affect this cyclization. Furthermore, primary and tertiary nucleophilic alcohol functions can be employed.

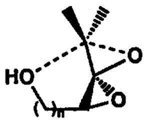
Insofar as *endo* cyclization of intermediates **30** is concerned, transition state **II** (n=2) appears to be quite reasonable. Of course, this requires the correct *anti* relationship of the side-chain and the oxygen of the more remote epoxide ring. This is expected to be the situation in most cases, provided that the spirodioxide stereochemistry is determined by steric effects in a fashion similar to that observed with simple allenes.[3] Any spirodioxide with inappropriate stereochemistry presumably is hydrolyzed by bimolecular reaction with water.

This scenario implies that the hydroxy group does not greatly influence the epoxidation stereochemistry at the remote double bond, since this would tend to produce the wrong *syn* stereochemistry. (Hydroxyl direction is well established for the peracid oxidations of olefinic alcohols.[14]) The clean *endo* cyclization of the terminal β-allenic alcohol **12b** supports the proposed mechanistic pathway, since alternate carbocationic intermediates are not likely with this substitution pattern. Likewise the 2.5:1 ratio of diastereomeric cyclic alcohols **13d** obtained from **12d** is consistent with expectations for a mixture of isomeric spirodioxides **30i** similar to the 2.2:1 mixture observed for the corresponding TBDMS ether **12i**. Oxidative cyclization of alcohols **12** proceeds with essentially all substitution patterns about the spirodioxide unit in intermediates **30**. Likewise, the secondary alcohol **12f** also worked well, albeit without stereochemical discrimination.

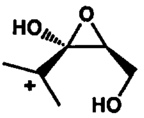
The situation with the α-alcohols appears to be different in that *endo* cyclization is observed only when the remote allenic carbon is mono- or disubstituted. This suggests the involvement of carbocationic intermediates of type III in the course of the cyclizations of spirodioxides **5**. A mechanistic change of this sort makes sense in view of the fact that a transition state of type II with n=1 (unlike the n=2 homolog) cannot reasonably achieve near colinearity of the forming and breaking C-O bonds owing to the restrictions of the shorter tether between the alcohol and spirodioxide moieties. However, opening of an *anti* spirodioxide to carbocation III releases enough of the geometrical constriction to permit intramolecular bond formation and subsequent ring-fission of the strained hemiacetal function. In the absence of carbocation-stabilizing substituents, this alternate cyclization mode is also retarded, permitting the slow hydrolysis by attack of traces of water on the unencumbered terminal epoxide of **5** to become a competitive process. Cyclization by an *exo* mode, another possibility for the spirodioxides derived from α- and β-allenic alcohols, has been observed only in the case of the oxidation of **2c**, where substitution by the very influential methoxy group provokes epoxide formation. Nonetheless, further examples can be anticipated in favorable circumstances.



I



II



III

Unfortunately, the analogous cyclizations of silyl ethers are much less general, owing to the more rigorous conditions required to promote them. This allows the incursion of other spirodioxide reactions, especially as the substitution of this unit increases. Thus, isomeric oxetanones and conjugated ketones are formed under these circumstances. On the other hand, hydrolysis becomes more important with less substituted spirodioxide intermediates. The mechanistic features of the cyclizations of silyl ethers are not understood, but catalysis by R_3Si^+ is a possibility, perhaps promoted by the presence of R_3SiCl, *etc.* as impurities in the starting allenic ethers. Interestingly, the same dichotomy for the α- and β-allenic alcohols is observed, such that terminal substitution is required for cyclization of the former, whereas unsubstituted examples of the latter work best.

Acknowledgement. The much earlier unpublished work of Dr. Woody Conover provided an important base for this study. This work was supported by a grant from the PHS (GM-39988). Departmental equipment grants aided in the purchase of the Varian XL-300 NMR (PHS SID-RR-1882), the Brucker AM-500 NMR (NSF CHE-85-1307; PHS SIO-RR-02858), and the Kratos MS 80 mass spectrometer (NSF CHE-81-11957).

EXPERIMENTAL

General. Infrared (IR) spectra were determined as thin films between NaCl discs or as solutions in $CDCl_3$ on a Perkin-Elmer Model 298 grating spectrometer or a Mattson Galaxy 4020 FT-IR instrument. Nuclear magnetic resonance (NMR) spectra were recorded on $CDCl_3$ solutions, unless otherwise specified, on a Varian XL-300 spectrometer (^1H at 300 MHz and ^{13}C at 75 MHz) or a Bruker AM-500 spectrometer (^1H at 500 MHz and ^{13}C at 125 MHz). The multiplicities of ^{13}C signals were determined by APT or DEPT techniques or by recording proton-coupled spectra. Coupling constants from the latter are given only when they deviate significantly from simple aliphatic hydrocarbon values. Mass spectra (MS) were obtained on a Kratos MS 80 RFAQQ spectrometer using chemical (CI) or electron-impact (EI) ionization. Exact-mass measurements are reported for the (M+1) or (M) peak unless otherwise specified. Melting points were determined on a Thomas-Hoover Unimelt apparatus. Analytical gas chromatography (GC) was performed on a Varian 3700 instrument fitted with a 50 m x 0.25 mm DB-5 fused silica capillary column, a flame-ionization detector, and a Hewlett-Packard model 3390-A integrator. Preparative GC was performed on an Aerograph A700 instrument. Preparative thin-layer chromatography (TLC) was performed on Kieselgel 60 F-254 silica gel on 10 x 20 cm plates of 0.25 mm thickness. Anhydrous diethyl ether was used directly from Mallinkrodt anhydrous ether cans. Tetrahydrofuran (THF) was distilled from sodium and benzophenone. Reagent grade acetone was used in the preparation of solutions of dimethyldioxirane (**1**) as previously described.[3] Allenic alcohols were prepared by the known procedure or general method referenced and were fully characterized.

Oxidation of 4-Methyl-2,3-pentadien-1-ol (2a). To 70 mg of **2a**[15] was added 65 mL (9 eq) of **1** in acetone. After 5 min, the acetone was removed and the residue was diluted with ether, dried ($MgSO_4$), and concentrated. Preparative TLC with 1:9 $MeOH/CHCl_3$ afforded 51 mg (55%) of 5-hydroxy-2,2-dimethyl-3-oxacyclopentanone (**3a**) as a colorless liquid: IR 3400, 1767 cm^{-1}; ^1H NMR (C_6D_6) δ 3.96 (distorted t, 1, $J = 9$ Hz), 3.81 (td, 1, $J = 9, 2$ Hz), 3.46 (distorted t, 1, $J = 9$ Hz), 2.29 (br d, 1, $J = 2$ Hz), 1.06 (s, 3), 1.01 (s, 3); ^{13}C NMR δ 218.1 (s), 79.0 (q, $J = 4$ Hz), 71.3 (d, $J = 145$ Hz), 67.0 (ddd, $J = 155, 145, 4$ Hz), 24.1 (qq, $J = 130, 6$ Hz), 21.8 (qq, $J = 130, 2$ Hz); MS(CI) *m/z* (rel intensity) 131 (33), 113 (8), 101 (5), 87 (17), 73 (5), 71 (36), 59 (100); exact mass 131.070, calcd for $C_6H_{11}O_3$ 131.0708. In another experiment a small amount (10% yield) of a polar compound was also isolated and tentatively assigned as 1,3,4-trihydroxy-3-methyl-2-butanone (**4a**): ^1H NMR δ 4.76 (X of ABX, 1, $J_{AX} = J_{BX} = 5$ Hz), 3.99 (AB of ABX, 2, $\delta_A = 3.86$, $\delta_B = 4.13$, $J_{AB} = 11$ Hz), 2.6-1.8 (br s, 3), 1.45 (s, 3), 1.43 (s, 3). This material was generally present in small amounts in other oxidations of **2a**, but was not isolated. A characteristic IR band at 1818 cm^{-1} indicated a trace amount of **28a** in these reactions.

Isomerization of 3a. Silica gel was added to a solution of 29 mg of **3a** in 2:1 ether/$CHCl_3$ until a thick slurry was obtained. After stirring for 6 h, filtration and concentration gave a 1:1 mixture of **3a** and a new compound assigned as 5-hydroxy-4,4-

dimethyl-3-oxacyclopentanone (15): ^{1}H NMR δ 4.22 (dd, 1, J = 17, 1.5 Hz), 4.06 (d, 1, J = 1.5 Hz), 3.95 (d, 1, J = 17 Hz), 1.52 (s, 3), 1.11 (s, 3). The IR spectrum of the mixture showed bands at 3430, 1772 cm^{-1}. The isomers were not separated by TLC.

Oxidation of 2a in the Presence of *p*-Toluenesulfonic Acid. To a stirred solution of 30 mg of **2a** in 20 mL of dry CH_2Cl_2 was added 9 mL (3 eq) of **1** containing 29 mg (0.5 eq) of TsOH over a 5-min period. After 10 min at room temperature, the mixture was washed with satd $NaHCO_3$ soln and water, and dried (K_2CO_3). Concentration gave 19 mg of a clear, colorless liquid containing 2,2-dimethyl-3-oxacyclopentanone (7) as the major product (*ca.* 80%), along with 5% of **3a** and 10% of 2-hydroxy-2-methylpent-4-en-3-one (8):[16] ^{1}H NMR δ 6.64 (AB of ABX, 2, δ_A = 6.69, δ_B = 6.59, J_{AB} = 17 Hz), 5.84 (X of ABX, 1, J_{AX} = 2 Hz, J_{BX} = 10 Hz), 3.84 (s, 1), 1.39 (s, 6). A pure sample of 7 was obtained by preparative GC: ^{1}H NMR δ 4.14 (t, 2, J = 7 Hz), 2.55 (t, 2, J = 7 Hz), 1.23 (s, 6); IR 1760, 1102 cm^{-1}. *Anal.* Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.0; H, 8.8.

Oxidation of 2-Methyl-2,3-butadien-1-ol (2b). To 50 mg of **2b**[17] was added 50 mL (8 eq) of **1**. After 10 min, the acetone was evaporated and the residue was evacuated to 0.2 torr to yield 72 mg (89%) of 1,3,4-trihydroxy-3-methyl-2-butanone (**4b**) as a clear, colorless liquid: IR 3390, 1705, 1049, 1018 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 4.53 (AB, 2, $\Delta\nu$ = 21 Hz, J = 20 Hz), 4.0-3.8 (br s, 3), 3.59 (AB, 2, $\Delta\nu$ = 75 Hz, J = 11 Hz), 1.21 (s, 3); ^{13}C NMR (acetone-d_6) δ 215.4 (s), 80.0 (s), 68.9 (tq, J = 142, 3 Hz), 66.5 (t, J = 144 Hz), 22.1 (q); MS(CI) *m/z* (rel intensity) 135 (46), 121 (15), 117 (38), 99 (96), 87 (65), 75 (100), 71 (22); exact mass 135.068, calcd for $C_5H_{11}O_4$ 135.0657.

Oxidation of 3-Methoxy-2-methyl-3,4-pentadien-2-ol (2c). A mixture of 68 mg of **2c**,[18] 5 g of anhydrous K_2CO_3, and 25 mL of **1** was stirred at room temperature for 15 min. The mixture was filtered, dried ($MgSO_4$) and concentrated to give 72 mg (85%) of a yellow liquid which consisted of **10** and **11** in a ratio of 1:3. 3,4-Epoxy-1-hydroxy-3-methoxy-4-methyl-2-pentanone (11) showed: ^{1}H NMR δ 4.60 (d, 1, J = 20 Hz), 4.39 (d, 1, J = 20 Hz), 3.38 (s, 3), 2.97 (br s, 1), 1.41 (s, 3), 1.19 (s, 3); ^{13}C NMR δ 204.8 (s), 89.7 (s), 68.1 (t), 66.8 (s), 54.1 (q), 19.2 (q), 18.8 (q); GC-MS (EI) *m/z* (rel intensity) 145 (4), 142 (1), 129 (1), 117 (4), 101 (17), 73 (100); exact mass 145.049, calcd for $C_6H_9O_4$ (M-CH_3) 145.0500. 3,4-Epoxy-3-methoxy-4-methyl-2-pentanone (10) was isolated by chromatography on silica gel using 10:1 ether-pentane and showed: IR 1728 cm^{-1}; ^{1}H NMR δ 3.38 (s, 3), 2.30 (s, 3), 1.40 (s, 3), 1.18 (s, 3); ^{13}C NMR δ 202.9 (s), 91.1 (s), 65.8 (s), 53.7 (q), 27.8 (q), 19.0 (q), 18.9 (q); GC-MS (EI) *m/z* (rel intensity) 129 (4), 112 (1), 102 (24), 101 (8), 87 (11), 73 (100); exact mass 129.056, calcd for $C_6H_9O_3$ (M-Me) 129.0551.

To a stirred solution of 23 mg of this mixture and 35 mg of imidazole in 4 mL of DMF was added 90 mg of *tert*-butyldimethylsilyl chloride (TBDMSCl). After 0.5 h, water was added and the mixture was extracted with CH_2Cl_2. The extracts were washed with water, dried ($MgSO_4$), and concentrated. Chromatography with 1:4 ether/pentane gave the TBDMS ether of 11 as a colorless liquid: IR 1740, 1256, 1136, 836 cm^{-1}; ^{1}H NMR δ 4.58

(d, 1, J = 19 Hz), 4.45 (d, 1, J = 19 Hz), 3.37 (s, 3), 1.40 (s, 3), 1.19 (s, 3), 0.90 (s, 9), 0.08 (s, 3), 0.07 (s, 3); ^{13}C NMR δ 202.6 (s), 90.0 (s), 68.7 (t), 66.0 (s), 53.9 (q), 25.7 (q), 19.4 (q), 19.0 (q), 18.5 (s), -5.4 (q), -5.5 (q); MS (CI) *m/z* (rel intensity) 259 (2), 243 (7), 187 (65), 173 (12), 159 (44), 143 (35), 117 (79), 89 (100), 73 (95); exact mass (M-CH_3) 259.136, calcd for $C_{12}H_{23}O_4Si$ 259.1366.

Oxidation of 2-Methyl-3,4-octadien-2-ol (2d). Reaction of 74 mg of **2d**[15] and 32 mL of **1** gave 50 mg (56%) of a 1:2 mixture of *cis*- and *trans*-5-hydroxy-4,4-dimethyl-2-propyl-3-oxacyclopentanone (**3d**) as major products: MS (CI) *m/z* (rel intensity) 173 (9), 155 (5), 114 (45), 72 (100); exact mass 173.119, calcd for $C_9H_{17}O_3$ 173.1178. ***Cis* 3d** showed: IR 3428, 1766, 1127, 1058, 1027 cm^{-1}; ^{1}H NMR δ 4.14 (ddd, 1, J = 9, 4.5, 2 Hz), 4.11 (dd, 1, J = 3, 2 Hz), 2.63 (d, 1, J = 3 Hz), 1.73 (m, 1), 1.58-1.39 (m, 2), 1.46 (s, 3), 1.31-1.2 (m, 1), 1.10 (s, 3), 0.92 (t, 3, J = 7 Hz); ^{13}C NMR δ 216.2, 80.1, 79.9, 76.4, 35.2, 27.3, 22.8, 19.1, 13.7. ***Trans* 3d** showed: IR 3388, 1768, 1124, 1026, 902 cm^{-1}; ^{1}H NMR δ 3.97 (d, 1, J = 3 Hz), 3.90 (dd, 1, J = 7, 5 Hz), 2.63 (d, 1, J = 3 Hz), 1.62 (m, 2), 1.48 (s, 3), 1.5-1.2 (m, 2), 1.08 (s, 3), 0.91 (t, 3, J = 7 Hz); ^{13}C NMR δ 218.0, 80.8, 79.5, 76.6, 33.9, 26.9, 19.4, 18.2, 13.8.

Oxidation of 5-Methyl-3,4-hexadien-1-ol (12a). A 22-mg sample of **12a**[19] and 12 mL (6 eq) of **1** gave 26 mg (92%) of 6-hydroxy-2,2-dimethyl-3-oxacyclohexanone (**13a**) as a colorless liquid: IR 3425, 1720, 1158, 1076 cm^{-1}; ^{1}H NMR δ 4.55 (dd, 1, J = 12, 7 Hz), 4.05 (ddd, 1, J = 13, 12, 4 Hz), 3.87 (ddd, 1, J = 13, 5, 2 Hz), 3.8-3.2 (br s, 1), 2.51 (m, 1), 1.99 (m, 1), 1.39 (s, 3), 1.37 (s, 3); decoupling at 3.87 gave 2.51 (ddd, J = 9, 7, 1.5 Hz), decoupling at 2.51 gave 4.55 (d, J = 12 Hz), 4.05 (dd, J = 13, 12 Hz) and 3.87 (dd, J = 13, 5 Hz); ^{13}C NMR δ 212.0 (s), 80.3 (br s), 70.1 (dm, J = 140 Hz), 59.0 (ddd, J = 146, 140, 6 Hz), 36.3 (t), 23.8 (q), 22.6 (qq, J = 125, 4 Hz); MS(EI) *m/z* (rel intensity) 145 (14), 127 (9), 116 (10), 99 (2), 87 (11), 85 (5), 83 (100), 71 (3); exact mass 145.086, calcd for $C_7H_{13}O_3$ 145.0865.

2-Hydroxy-3,3-dimethyl-4-oxacyclohexanone (14). To a stirred solution of 22 mg of **13a** in 15 mL of ether and 7.5 mL of $CHCl_3$ was added silica gel until a thick slurry was formed. The slurry was stirred for 5 h and then applied directly onto the top of a column of silica gel and eluted with 4:1 ether-hexane to give 14 mg (63%) of **14** as a yellow liquid: IR 3480, 1713, 1223, 1104 cm^{-1}; ^{1}H NMR δ 4.09 (ddd, 1, J = 12, 9, 1.5 Hz), 4.02 (dd, 1, J = 4, 1.5 Hz), 3.85 (td, 1, J = 12, 3 Hz), 3.62 (d, 1, J = 4 Hz), 2.76 (dddd, 1, J = 14, 12, 9, 1.5 Hz), 2.45 (ddd, 1, J = 14, 3, 1.5 Hz), 1.43 (s, 3), 1.04 (s, 3); decoupling at 2.45 gave 4.09 (dd, J = 12, 9 Hz), 3.85 (t, J = 12 Hz), decoupling at 2.76 gave 4.02 (d, J = 4 Hz); ^{13}C NMR δ 207.8 (s), 81.1 (d, J = 146 Hz), 80.5 (s), 60.9 (tm, J = 147 Hz), 40.3 (t, J = 128 Hz), 27.8 (qm, J = 126 Hz), 17.3 (qm, J = 127 Hz); MS(CI) *m/z* (rel intensity) 145 (13), 129 (4), 99 (4), 86 (100), 84 (48), 73 (3); exact mass 145.086, calcd for $C_7H_{13}O_3$ 145.0865.

Oxidation of 12a in the Presence of *p*-Toluenesulfonic Acid. To a stirred solution of 30 mg of **12a** in 20 mL of dry CH_2Cl_2 was added 8 mL (3 eq) of **1** in acetone containing 25 mg (0.5 eq) of TsOH. After 10 min at room temperature, the mixture was washed with satd $NaHCO_3$ soln and water, dried (K_2CO_3), and concentrated to afford 27 mg (79%) of 2,2-dimethyl-3-oxacyclohexanone (**16a**) as a clear, colorless liquid:[7] IR 1717, 1087 cm^{-1}; ^1H NMR δ 3.86 (t, 2, J = 7 Hz), 2.51 (t, 2, J = 7 Hz), 2.07 (quintet, 2, J = 7 Hz), 1.32 (s, 6). ***Anal.*** Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.6; H, 8.9. Approximately 10% of **13a** was present in the crude product by NMR.

Oxidation of 2,2-Dimethyl-3,4-pentadien-1-ol (12b). Reaction of 20 mg of **12b**[20] and 18 mL (10 eq) of **1** gave 25 mg (96%) of 6-hydroxy-5,5-dimethyl-3-oxacyclohexanone (**13b**) as a colorless liquid: IR 3460, 1727, 1248, 1106 cm^{-1}; ^1H NMR δ 4.13 (dd, 1, J = 14.4, 0.5 Hz), 4.02 (br s, 1), 4.00 (dd, 1, J = 14.4, 1.2 Hz), 3.63 (AB, 2, $\Delta\nu$ = 15, Hz, J = 12 Hz), 3.5-3.4 (br s, 1), 1.08 (s, 3), 0.94 (s, 3); ^{13}C NMR δ 206.9, 81.0, 76.4, 72.7, 42.8, 22.6, 17.7; MS (CI) *m/z* (rel intensity) 145 (23), 144 (16), 127 (4), 101 (5), 85 (37), 71 (100); exact mass 145.087, calcd for $C_7H_{13}O_3$ 145.0864.

Oxidation of 3,5-Dimethyl-3,4-hexadien-1-ol (12c). Reaction of 55 mg of **12c**[21] and 26 mL of **1** gave 41 mg (65%) of 6-hydroxy-2,2,6-trimethyl-3-oxacyclohexanone (**13c**) as a white solid: mp 47-50°C; IR 3530, 1721, 1177, 1082, 1034 cm^{-1}; ^1H NMR δ 3.94 (ddd, 1, J = 12.3, 7.5, 4.8 Hz), 3.92 (ddd, 1, J = 12.3, 8.6, 7.1 Hz), 3.49 (s, 1), 2.18 (ddd, 1, J = 13.7, 6.1, 4.8 Hz), 2.09 (m, 1), 1.49 (d, 3, J = 0.6 Hz), 1.37 (s, 3), 1.35 (s, 3); decoupling at 1.49 gave 2.09 (ddd, J = 13.7, 8.6, 7.5 Hz); ^{13}C NMR δ 216.3, 80.3, 73.5, 58.3, 37.2, 26.4, 24.9, 24.5; MS (CI) *m/z* (rel intensity) 159 (12), 141 (19), 130 (18), 99 (6), 83 (10), 72 (100); exact mass 159.102, calcd for $C_8H_{15}O_3$ 159.1021.

Oxidation of 2,2-Dimethyl-3,4-octadien-1-ol (12d). Reaction of 16 mL (6 eq) of **1** and 40 mg of **12d**[20] gave 36 mg (75%) of a 2.5:1 mixture of *trans*- and *cis*-6-hydroxy-5,5-dimethyl-2-propyl-3-oxacyclohexanone (**13d**) as a colorless liquid: IR 3460, 1725, 1252, 1119, 1088 cm^{-1}; MS(CI) *m/z* (rel intensity) 187 (32), 169 (3), 131 (5), 114 (36), 86 (54), 71 (100), 69 (10); exact mass 187.133, calcd for $C_{10}H_{19}O_3$ 187.1334. ***Cis*** **13d** showed: ^1H NMR δ 3.97 (br d, 1, J = 3 Hz), 3.80 (ddd, 1, J = 8, 4, 1 Hz), 3.63 (AB, 2, $\Delta\nu$ = 17 Hz, J = 12 Hz), 3.47 (d, 1, J = 3 Hz), 1.06 (s, 3), 0.94 (t, 3), 0.88 (s, 3); ^{13}C NMR δ 207.5, 81.16, 80.3, 75.7, 44.0, 30.6, 22.5, 18.2, 17.7, 13.9. ***Trans*** **13d** showed: ^1H NMR δ 4.18 (d, 1, J = 3 Hz), 4.05 (dd, 1, J = 10, 6 Hz), 3.63 (AB, 2, $\Delta\nu$ = 222 Hz, J = 13 Hz), 3.33 (d, 1, J = 3 Hz), 1.11 (s, 3), 0.94 (t, 3), 0.91 (s, 3); ^{13}C NMR δ 211.3, 81.1, 78.5, 72.2, 41.9, 31.7, 23.8, 18.8, 18.3, 13.5.

Reaction of 30 mg of **13d** with TBDMS triflate in the usual manner gave 36 mg (75%) of a 2.5:1 mixture of *trans* and *cis* **13i** as a clear, colorless liquid: IR 1731, 1254, 1089 cm^{-1}; MS(CI) *m/z* (rel intensity) 243 (7), 213 (6), 171 (100), 115 (4), 86 (13), 75 (26); exact mass 243.142, calcd for $C_{12}H_{23}O_3Si$ (M-*t*Bu) 243.1416. The *cis* isomer showed: ^1H NMR δ 3.94 (d, 1, J = 1 Hz), 3.70 (m, 1, partially obscured, but J = 1 Hz apparent), 3.62 (AB, 2, $\Delta\nu$ = 12 Hz, J = 11 Hz), 0.12 (s, 3), 0.00 (s, 3). The *trans* isomer showed: ^1H NMR δ 4.09 (dd, 1, J = 8, 5 Hz), 3.71 (s, 1), 3.59 (AB, 2, $\Delta\nu$ = 143 Hz, J = 11 Hz), 0.04 (s, 3), 0.02 (s, 3).

Oxidation of 3,4-Octadien-1-ol (12e). Reaction of 60 mg of **12e**[20] and 29 mL of **1** in acetone gave 59 mg (67%) of 6-hydroxy-2-propyl-3-oxacyclohexanone (**13e**) as a colorless liquid: IR 3435, 1730, 1257, 1176, 1086 cm^{-1}. ^{1}H NMR showed a 1.2:1 mixture of *trans* and *cis*-13e as determined by the integrals of signals at δ 4.52 (dd, J = 11, 8 Hz) and 4.29 (ddd, J = 12, 7, 1 Hz), respectively.

This mixture was silylated with TBDMSCl in the usual manner to give a mixture of *trans* and *cis* 13k as a colorless liquid: IR 1740, 1259, 1098 cm^{-1}; MS (CI) *m/z* (rel intensity) 273 (1), 215 (33), 187 (4), 159 (4), 143 (100), 101 (27); exact mass 273.187, calcd for $C_{14}H_{29}O_3Si$ 273.1885. The *trans* isomer showed: ^{1}H NMR δ 4.33 (dd, 1, J = 7, 5.5 Hz), 4.09 (dd, 1, J = 8, 5 Hz), 3.92 (m, 2), 1.97 (m, 1), 1.67 (m, 1), 0.88 (s, 9), 0.06 (s, 3), 0.04 (s, 3). The *cis* isomer showed: ^{1}H NMR δ 4.26 (dd, 1, J = 12, 7, 1 Hz), 4.05 (ddd, 1, J = 12, 5, 2 Hz), 3.76 (td, 1, J = 12, 2 Hz), 3.73 (ddd, 1, J = 8, 4, 1 Hz), 2.14 (m, 1), 1.78 (m, 1), 0.88 (s, 9), 0.13 (s, 3), 0.03 (s, 3); ^{13}C NMR δ 205.5, 82.0, 74.9, 65.0, 38.6, 30.9, 25.7, 18.6, 18.4, 14.0, -4.6, -5.4. Overlapping ^{1}H signals at δ 2.31, 1.54, 1.38, and 0.91 are common to both isomers.

Oxidation of 6-Methyl-4,5-heptadien-2-ol (12f). Reaction of 84 mg of 12f^{22} with 40 mL of 1 gave 85 mg (80%) of 6-hydroxy-2,2,4-trimethyl-3-oxacyclohexanone (13f) as a 1.3:1 mixture of diastereomers: IR 3499, 1724, 1383, 1061 cm^{-1}; MS (CI) *m/z* (rel intensity) 159 (32), 141 (24), 117 (14), 100 (60), 87 (48), 72 (100); exact mass 159.101, calcd for $C_8H_{15}O_3$ 159.1021. *Trans* 13f showed: ^{1}H NMR δ 4.67 (t, 1, J = 9.6 Hz), 4.00 (m, 1), 2.40 (ddd, 1, J = 13.2, 9.6, 6.6 Hz), 2.16 (s, 1), 1.86 (ddd, 1, J = 13.2, 9.6, 7.4 Hz), 1.38 (s, 3), 1.32, (d, 3, J = 6.2 Hz), 1.31 (s, 3); ^{13}C NMR δ 217.4, 80.5, 68.6, 65.0, 39.1, 26.2, 22.7, 21.5. *Cis* 13f showed: ^{1}H NMR δ 4.50 (dd, 1, J = 12.5, 7 Hz), 4.24 (dqd, 1, J = 12.5, 6.1, 1.8 Hz), 2.45 (ddd, 1, J = 12.5, 7, 1.8 Hz), 2.43 (s, 1), 1.73 (q, 1, J = 12.5 Hz), 1.39 (s, 3), 1.33 (s, 3), 1.25 (d, 3, J = 6.1 Hz); ^{13}C NMR δ 211.2, 79.1, 69.7, 64.9, 44.8, 24.7, 22.6, 21.2.

Oxidation of 2,2,5-Trimethyl-3,4-hexadien-1-ol (12g). A. Reaction of 84 mg of 12g^{20} with 20 mL of 1 gave 74 mg (72%) of 6-hydroxy-2,2,5,5-tetramethyl-3-oxacyclohexanone (13g) as a white, crystalline solid: mp 84-85°C; IR 3500, 1720, 1040 cm^{-1}; ^{1}H NMR δ 4.20 (d, 1, J = 4 Hz), 3.64 (AB, 2, Δν = 128 Hz, J = 13 Hz), 3.48 (d, 1, J = 4 Hz), 1.39 (s, 3), 1.34 (s, 3), 1.08 (s, 3), 0.89 (s, 3); ^{13}C NMR δ 211.3, 79.2, 78.1, 70.5, 43.5, 24.2, 22.9, 22.1, 17.7; MS (CI) *m/z* (rel intensity) 155 (3), 114 (3), 86 (45), 71 (100); exact mass 173.118, calcd for $C_9H_{17}O_3$ 173.1178.

B. A solution of 10 g of Oxone, 25 g of $NaHCO_3$, 0.1 g of 18-Crown-6 and 130 mg of 12g in 2 mL of acetone, 20 mL of benzene and 20 mL of water was stirred for 4 h in an ice bath. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were dried ($MgSo_4$), concentrated and separated by chromatography on silica gel using 2:1 hexane/ether to give 53 mg (33%) of 13g and 15 mg (10%) of 2,2,5,5-tetramethyl-3-oxacyclohexanone (16g) as an oil: IR 1718, 1080 cm^{-1}; ^{1}H NMR δ 3.55 (s, 3), 2.30 (s, 3), 1.32 (s, 6), 1.01 (s, 6); MS (EI) *m/z* (rel intensity) 156 (4), 113 (12), 70 (100), 59 (40), 55 (100); exact mass 156.117, calcd for $C_9H_{16}O_2$ 156.1151.

C. A similar experiment using 100 (mg) of 12g, 15 g of Oxone and 0.1 g of

18-Crown-6 in 2 mL of acetone, 50 mL of water and 40 mL of CH_2Cl_2 gave 23 mg (18%) of **13g** and 48 mg (44%) of **16g**.

D. An experiment with 1 g of **12g**, 73 g of Oxone, 20 g of $NaHCO_3$, 0.7 g of Bu_4NHSO_4 in 15 mL of acetone, 225 mL of water, and 180 mL of CH_2Cl_2 gave a 24% yield of **13g** and a 28% yield of **16g**. A procedure omitting the Bu_4NHSO_4 gave 21% of **13g** and 28% of **16g**.

E. An experiment using 1 g of **12g**, 73 g of Oxone, 20 g of $NaHCO_3$, 5 mL of trifluoroacetone, 30 mL of CH_2Cl_2 and 225 mL of H_2O at 0°C for 18 h gave 40% of **13g** and 22% of **16g**.

Oxidation of 6-Methyl-4,5-heptadien-1-ol (17a). A 35-mg sample of **17a**[23] and 10 mL (3.3 eq) of **1** gave 39 mg (88%) of 2-(2-hydroxy-2-methyl-1-oxopropyl)tetrahydrofuran (**18a**) as a clear, colorless liquid: IR 3449, 1715, 1174, 1037, 729 cm^{-1}; ^1H NMR (C_6D_6) δ 4.43 (dd, 1, J = 7, 6 Hz), 3.8 (br s, 1), 3.6-3.4 (m, 2), 1.9-1.6 (m, 2), 1.5-1.2 (m, 8, including singlets at 1.35 and 1.31); decoupling at 1.3 gave 3.53 (AB, $\Delta\nu$ = 18 Hz, J = 8 Hz), decoupling at 1.75 gave 4.43 (s); ^{13}C NMR (C_6D_6) δ 213.2 (s), 80.8 (d, J = 150 Hz), 77.0 (br s), 69.1 (t, J = 145 Hz), 28.9 (t), 26.8 (q), 26.6 (q), 25.5 (t); MS(CI) *m/z* (rel intensity) 159 (2), 141 (2), 131 (8), 113 (2), 100 (22), 71 (88), 59 (100); exact mass 159.102, calcd for $C_8H_{15}O_3$ 159.1022.

Oxidation of 17a in the Presence of *p*-Toluenesulfonic Acid. To a stirred solution of 120 mg (4 eq) of TsOH in 2 mL of acetone and 15 mL of CH_2Cl_2 was added 20 mg of **17a**. A mixture of 5 mL (3 eq) of **1** in acetone and 10 mL of CH_2Cl_2 was added dropwise to the reaction over a period of 1.7 h. The mixture was washed with satd $NaHCO_3$ soln and water, dried (K_2CO_3), and concentrated to give a 5:1 mixture of 2-(2-methyl-1-oxopropyl tetrahydrofuran (**19**) and **18a**. Preparative TLC using 1:3 ether/hexane gave 11 mg (50%) of **19** as a colorless liquid: IR 2978, 2936, 2878, 1712, 1449, 1076, 1021 cm^{-1}; ^1H NMR δ 4.44 (m, 1), 4.0-3.8 (m, 2), 2.96 (septet, 1, J = 7 Hz), 2.3-2.1 (m, 1), 2.0-1.8 (m, 3), 1.12 (d, 3, J = 7 Hz), 1.08 (d, 3, J = 7 Hz); MS(EI) *m/z* (rel intensity) 142 (2), 125 (2), 119 (25), 113 (3), 100 (3), 71 (100); exact mass 142.096, calcd for $C_8H_{14}O_2$ 142.0994.

Oxidation of 4-Methyl-4,5-hexadien-1-ol (17b). A 70-mg sample of **17b**[24] and 45 mL (7.5 eq) of **1** yielded 43 mg (48%) of 2-(2-hydroxy-1-oxoethyl)-2-methyltetrahydrofuran (**18b**) as a clear liquid: IR 3440, 1717, 1112, 1039, 1004 cm^{-1}; ^1H NMR δ 4.48 (AB, 2, $\Delta\nu$ = 50 Hz, J_{AB} = 20 Hz), 4.0-3.8 (m, 2), 3.0-2.8 (br s, 1), 2.3-1.7 (m, 4), 1.35 (s, 3); ^{13}C NMR δ 214.9 (br s), 87.5 (s), 69.1 (t, J = 146 Hz), 65.1 (t, J = 147 Hz), 35.9 (t), 25.7 (t), 24.1 (q); MS(CI) *m/z* (rel intensity) 145 (18), 129 (5), 127 (7), 85 (100); exact mass 145.087, calcd for $C_7H_{13}O_3$ 145.0865.

Oxidation of 2,7-Dimethyl-5,6-octadien-2-ol (17c). Reaction of 70 mg of **17c**[25] with 28 mL of **1** gave 59 mg (70%) of 2-(2-hydroxy-2-methyl-1-oxopropyl)-5,5-dimethyl-tetra-hydrofuran (**18c**) as an oil: IR 3450, 1722 cm^{-1}; ^1H NMR δ 4.76 (t, 1, J = 7.5 Hz), 4.0 (br s, 1), 2.3-2.2 (m, 1), 2.2-2.1 (m, 1), 1.75 (t, 2, J = 7.5 Hz); 1.37 (s, 3), 1.36 (s, 3), 1.30 (s, 3), 1.25 (s, 3); ^{13}C NMR δ 213.3, 83.4, 80.6, 77.2, 37.7, 29.2, 28.1, 27.5, 26.8, 26.6; MS (CI) *m/z* (rel intensity) 187 (47), 169 (18), 129 (100), 99 (93), 81 (59); exact mass 187.132, calcd for $C_{10}H_{19}O_3$ 187.1334.

Oxidation of 7-Methyl-5,6-octadien-1-ol (20a). A 50-mg sample of **20a**[26] and 55 mL (15 eq) of **1** gave 56 mg (75%) of 2-(2-hydroxy-2-methyl-1-oxopropyl)tetrahydropyran (**21a**) as a colorless liquid: IR 3460, 1715, 1442, 1353, 1256, 1079, 1044 cm^{-1}; ^1H NMR δ 4.2-3.7 (m, 3), 3.47 (td, 1, J = 11, 3 Hz), 1.90 (m, 2), 1.7-1.5 (m, 4), 1.38 (s, 6); ^{13}C NMR δ 211.6 (s), 81.8 (d, J = 140 Hz), 77.5 (br s), 68.7 (t, J = 140 Hz), 28.3 (t), 26.3 (q), 25.4 (t), 22.8 (t); MS(CI) *m/z* (rel intensity) 173 (0.1), 154 (1), 129 (9), 114 (20), 85 (86), 59 (100); exact mass 173.118, calcd for $C_9H_{17}O_3$ 173.1178.

Oxidation of 5-Methyl-5,6-heptadien-1-ol (20b). A 60-mg sample (0.5 mmol) of **20b**[27] and 50 mL (10 eq) of **1** gave 49 mg (65%) of 2-(2-hydroxy-1-oxoethyl)-2-methyltetra- hydropyran (**21b**) as a clear, colorless liquid: IR 3450, 1720, 1213, 1084, 1049, 1010 cm^{-1}; ^1H NMR δ 4.49 (s, 2), 3.78 (m, 1), 3.51 (m, 1), 3.0-2.8 (br s, 1), 2.0-1.4 (m, 6), 1.30 (s, 3); ^{13}C NMR δ 214.1 (s), 80.0 (br s), 64.5 (t, J = 145 Hz), 63.8 (t, J = 141 Hz), 31.9 (t), 25.1 (t), 23.0 (q), 19.5 (t); MS(CI) *m/z* (rel intensity) 159 (2), 141 (15), 123 (2), 113 (5), 99 (100), 71 (6); exact mass 159.108, calcd for $C_8H_{15}O_3$ 159.1021.

Oxidation of 5,6-Heptadien-1-ol (20c). A 50-mg sample of **20c**[28] and 40 mL (9 eq) of **1** afforded 35 mg (55%) of 2-(2-hydroxy-1-oxoethyl)tetrahydropyran (**21c**) as a clear, colorless liquid: IR 3430, 1722, 1263, 1208, 1081, 1051 cm^{-1}; ^1H NMR δ 4.46 (AB, 2, $\Delta\upsilon$ = 9 Hz, J = 20 Hz), 4.01 (dm, 1, J = 11 Hz), 3.94 (dd, 1, J = 11, 2 Hz), 3.44 (td, 1, J = 11, 3 Hz), 3.0 (br s, 1), 1.89 (m, 2), 1.54 (m, 4); ^{13}C NMR δ 210.5 (s), 81.3 (d, J = 140 Hz), 68.2 (t, J = 141 Hz), 65.6 (t, J = 146 Hz), 28.3 (t), 25.4 (t), 22.7 (t); MS(CI) *m/z* (rel intensity) 145 (10), 127 (65), 99 (12), 85 (100), 71 (7); exact mass 145.086, calcd for $C_7H_{13}O_3$ 145.0865.

Oxidation of 8-Methyl-6,7-nonadien-1-ol (22a). A 50-mg sample (0.3 mmol) of **22a**[29] and 35 mL (10 eq) of **1** gave 22 mg (36%) of 2,4,9-trihydroxy-2-methyl-3-nonanone (**25a**, X = OH), 14 mg (23%) of 4,9-dihydroxy-2-methylnon-1-en-3-one (**23**), and 8 mg (13%) of 4-(5-hydroxypentyl)-2,2-dimethyl-3-oxetanone (**24a**). Compound **25a** showed: IR 3390, 1705, 1183, 1043 cm^{-1}; ^1H NMR δ 4.64 (dd, 1, J = 7, 3 Hz), 3.63 (t, 2, J = 7 Hz), 3.0 (br s, 3), 2.0-1.2 (m, 14, including singlets at 1.39 and 1.42); MS(CI) *m/z* (rel intensity) 205 (2), 187 (3), 169 (12), 151 (3), 129 (58), 115 (47), 99 (30), 87 (10), 83 (100), 69 (22); exact mass 205.148, calcd for $C_{10}H_{21}O_4$ 205.1440. Compound **23** showed: IR 3415, 3101, 1670, 1629, 1047, 967 cm^{-1}; ^1H NMR δ 5.91 (br s, 2), 4.81 (dd, 1, J = 8,3 Hz), 3.64 (t, 2, J = 6 Hz), 2.35 (br s, 2), 1.94 (t, 3, J = 1.8 Hz), 1.9-1.2 (m, 8); MS(CI) *m/z* (rel intensity) 187 (7), 169 (11), 151 (3), 135 (3), 117 (24), 115 (30), 99 (62), 81 (100); exact mass 187.133, calcd for $C_{10}H_{19}O_3$ 187.1334. Compound **24a** showed: IR 3400, 1815, 1030 cm^{-1}; ^1H NMR δ 5.30 (t, 1, J = 7 Hz), 3.65 (t, 2, J = 7 Hz), 1.95-1.20 (m, 14, including singlets at 1.43 and 1.47). When the above oxidation was carried out using oxidant which had been dried three times over $CaSO_4$ and stored over 4 Å molecular sieves, the yields were: **25a** (5%), **23** (38%), and **24a** (33%).

Oxidation of 22a in the Presence of Potassium Carbonate. To a stirred mixture of 7 mL (5 eq) of **1** in acetone containing 2 g of K_2CO_3 was added 20 mg of **22a** in 0.2 mL of acetone. After 10 min the solvent was removed and the residue was diluted with ether, dried (K_2CO_3), and concentrated to give 23 mg (96%) of **26a** as a colorless liquid: ^1H NMR δ 3.74 (dd, 1, J = 6,5 Hz), 3.63 (t, 2, J = 7 Hz), 1.9-1.2 (m, 15, including singlets at 1.55 and 1.49).

2-(2-Hydroxy-2-methyl-1-oxopropyl)oxepane (27). A stirred solution of 37 mg of **26a**[29] in 5 mL of $CDCl_3$ containing 20 mg of K_2CO_3 was heated at 60°C for 10 days. ^1H NMR analysis showed complete conversion to **27** along with small amounts of **23** and **24a**. The mixture was filtered through Celite and concentrated. Preparative TLC using 3:1 ether/hexane gave 29 mg (78%) of **27** as a colorless liquid: IR 3460, 1719, 1123, 732 cm^{-1}; ^1H NMR δ 4.36 (dd, 1, J = 8, 5 Hz), 4.2-4.0 (br s, 1), 3.96 (ddd, 1, J = 12, 7, 4 Hz), 3.65 (ddd, 1, J = 12, 8, 5 Hz), 2.0-1.2 (m, 14, including singlets at 1.40 and 1.39); ^{13}C NMR δ 213.0 (s), 82.5 (d, J = 140 Hz), 77.4 (s), 69.4 (t, J = 142 Hz), 31.7 (t), 30.7 (t), 26.8 (t), 26.6 (q), 26.5 (q), 25.7 (t); MS(EI) *m/z* (rel intensity) 187 (0.2), 168 (0.6), 128 (18), 110 (25), 100 (40), 99 (100), 81 (89), 69 (8); exact mass 187.132, calcd for $C_{10}H_{19}O_3$ 187.1335, 168.115, calc for $C_{10}H_{16}O_2$ ($M-H_2O$) 168.1150.

Oxidation of 6-Methyl-6,7-octadien-1-ol (22b). A 58-mg sample (0.4 mmol) of **22b**[27] and 40 mL (10 eq) of **1** yielded 51 mg (66%) of 1,3,8-trihydroxy-3-methyl-2-octanone (**25b**; X = OH) as a clear liquid: IR 3390, 1713, 1262, 1050, 1014 cm^{-1}; ^1H NMR δ 4.49 (s, 2), 3.61 (t, 2, J = 6 Hz), 2.6-2.4 (br s, 3), 1.8-1.0 (m, 11, including a singlet at 1.36); ^{13}C NMR δ 214.4 (s), 78.4 (s), 64.7 (t, J = 146 Hz), 62.5 (t, J = 140 Hz), 39.9 (t), 32.2 (t), 25.8 (t), 25.7 (q), 22.9 (t); MS(CI) *m/z* (rel intensity) 173 (3), 155 (12), 131 (42), 113 (100), 95 (28), 85 (17), 71 (32); exact mass 173.116, calcd for $C_9H_{17}O_3$ ($M-H_2O$) 173.1178.

1-Acetoxy-3,8-dihydroxy-3-methyl-2-octanone (25b, X = OAc). A reaction of 25 mL (7 eq) of **1** in acetone containing 525 mg (15 eq) of potassium acetate and 50 mg of **22b** provided 48 mg (63%) of **25b** as a colorless liquid: IR 3430, 1732, 1235 cm^{-1}; ^1H NMR δ 4.96 (AB, 2, $\Delta\upsilon$ = 13 Hz, J = 17 Hz), 3.59 (t, 2, J = 6 Hz), 2.78 (s, 2), 2.16 (s, 3), 1.8-1.1 (m, 11, including a singlet at 1.36); ^{13}C NMR δ 207.7 (s), 170.5 (br s), 78.7 (s), 65.2 (t, J = 148 Hz), 62.4 (t, J = 139 Hz), 39.8 (t), 32.1 (t), 25.8 (t), 25.5 (q), 22.7 (t), 20.4 (q); MS(CI) *m/z* (rel intensity) 233 (4), 215 (16), 197 (7), 131 (54), 113 (100), 95 (18), 84 (5); exact mass 233.140, calcd for $C_{11}H_{21}O_5$ 233.1418.

1-*tert*-Butyldimethylsiloxy-2,2-dimethyl-3,4-octadiene (12h). To a stirred solution of 1.17 g (1.2 eq) of TBDMSCl and 0.57 g (1.3 eq) of imidazole in 6 mL of DMF containing 20 mg of DMAP at 0°C under nitrogen was added 1.0 g (6.5 mmol) of **12d** in 7 mL of CH_2Cl_2 dropwise over a period of 5 min. The reaction was stirred at 0°C for 0.5 h and at room temperature for 1 h. The mixture was washed with water, satd $CuSO_4$ soln, and brine, dried ($MgSO_4$) and concentrated. Column chromatography on silica gel with 4% ether in hexane gave 1.75 g (100%) of **12h** as a colorless liquid: IR 1962, 1253, 1093, 833 cm^{-1}; ^1H NMR δ 5.2-5.1 (m, 2), 3.30 (s, 2), 2.0-1.9 (m, 2), 1.43 (sextet, 2, J = 7

Hz), 0.97 (s, 6), 0.93 (t, 3, J = 7 Hz), 0.89 (s, 9), 0.03 (s, 3); MS(CI) *m/z* (rel intensity) 211 (100), 181 (14), 155 (8), 137 (16), 115 (30), 107 (10); exact mass 211.152, calcd for $C_{12}H_{23}OSi$ (M-tBu) 211.1551.

A similar procedure was utilized for the preparation of TBDMS ethers of other allenic alcohols. These compounds showed spectral properties in full accord with the indicated structures.

Oxidation of 1-*tert*-Butyldimethylsiloxy-4-methyl-2,3-pentadiene (2e). To a stirred solution of 5 mL (5 eq) of 1 in acetone containing 0.75 g of K_2CO_3 was added 20 mg of 2e. After 12 min at room temperature, the mixture was concentrated and the residue was diluted with ether, dried (K_2CO_3), and concentrated to afford 23 mg (100%) of 5e as a colorless liquid: IR 1641 cm^{-1}; ^1H NMR δ 3.95 (AB of ABX, 2, $\delta_A = 4.06$, $\delta_B = 3.84$, $J_{AB} = 12$ Hz), 3.82 (X of ABX, 1, $J_{AX} = 4$ Hz, $J_{BX} = 3$ Hz), 1.56 (s, 3), 1.49 (s, 3), 0.89 (s, 9), 0.08 (s, 3), 0.07 (s, 3).

5-*tert*-Butyldimethylsiloxy-2,2-dimethyl-3-oxacyclopentanone (3e). A mixture of 79 mg of 5e and 20 mg of $NaHCO_3$ in 3 mL of $CDCl_3$ was heated at 65°C for 2.5 h. The mixture was passed through Celite, concentrated, and purified by preparative TLC with 1:4 ether/hexane to provide 51 mg (65%) of 3e as a colorless liquid: IR 1772 cm^{-1}; ^1H NMR δ 4.35 (distorted t, 1, J = 9 Hz), 4.25 (distorted t, 1, J = 9 Hz), 3.70 (t, 1, J = 9 Hz), 1.26 (s, 3), 1.23 (s, 3), 0.89 (s, 9), 0.14 (s, 3), 0.10 (s, 3); ^{13}C NMR δ 215.9 (s), 78.9 (s), 72.1 (d, J = 142 Hz), 67.8 (ddd, J = 153, 146, 5 Hz), 25.7 (q of sept, J = 120, 5 Hz), 24.3 (qq, J = 128, 5 Hz), 21.9 (qq, J = 127, 5 Hz), 18.2 (s), -4.6 (q), -5.1 (q); MS (CI) *m/z* (rel intensity) 187 (40), 159 (59), 145 (22), 129 (85), 101 (100), 84 (56), 75 (81); exact mass 187.078, calcd for $C_8H_{15}O_3Si$ (M-tBu) 187.0811.

Oxidation of 1-*tert*-Butyldimethylsiloxy-2,3-butadiene (2f). Reaction of 56 mg of 2f and 25 mL of 1 gave 52 mg of a yellow liquid which was predominantly 4-*tert*-butyldimethylsilyloxy-1,3-dihydroxy-2-butanone (4f). Purification on silica gel using 3:1 ether/pentane gave 26 mg (37%) of 4f as a yellow liquid: IR 3434, 1726, 1256, 1113 cm^{-1}; ^1H NMR δ 4.57 (dd, 1, J = 20, 0.6 Hz), 4.39 (d, 1, J = 20 Hz), 4.27 (br t, 1), 3.91 (dd, 1, J = 10, 4 Hz), 3.77 (dd, 1, J = 10, 5 Hz), 3.3-2.7 (2), 0.84 (s, 9), 0.04 (s, 3), 0.03 (s, 3); decoupling at 4.27 gave 4.57 (d, J = 20 Hz), 3.91 (d, 1, J = 10 Hz), 3.77 (d, 1, J = 10 Hz); ^{13}C NMR δ 211.4 (s), 75.9 (d), 67.0 (t), 64.4 (t), 25.7 (q), 18.2 (s), -5.56 (q), -5.63 (q).

Oxidation of 1-*tert*-Butyldimethylsiloxy-2-methyl-2,3-butadiene (2g). Reaction of 26 mg of 2g and 15 mL of 1 gave 30 mg (100%) of a 2.2:1 mixture of *anti* and *syn* 5g as a colorless liquid: IR 1620, 1250, 1090, 832 cm^{-1}. The major isomer showed: ^1H NMR δ 3.81 (AB, 2, $\Delta\nu = 24$ Hz, J = 12 Hz), 3.51 (d, 1, J = 3 Hz), 3.33 (d, 1, J = 3 Hz), 1.53 (s, 3), 0.86 (s, 9), 0.04 (s, 3), 0.03 (s, 3); ^{13}C NMR δ 84.6 (s), 65.9 (s), 64.5 (t), 49.5 (t), 25.7 (q), 18.2 (s), 15.4 (q), -5.5 (q). The minor isomer showed: ^1H NMR δ 3.87 (AB, 2, $\Delta\nu = 6$ Hz, J = 12 Hz), 3.44 (d, 1, J = 3 Hz), 3.28 (d, 1, J = 3 Hz), 1.53 (s, 3), 0.89 (s, 9), 0.07 (s, 3), 0.05 (s, 3); ^{13}C NMR δ 85.4 (s), 65.3 (s), 65.0 (t), 47.9 (t), 25.8 (q), 18.3 (s), 16.6 (q), -5.5 (q).

Heating this sample in 7 mL of CCl_4 at reflux for 18 h in the presence of 1 g of $MgSO_4$ gave a complex mixture which appeared to contain **28g**: IR 1823 cm^{-1}; ^{1}H NMR δ 5.13 (AB, 2, J = 14 Hz), 3.72 (AB, 2, J = 12 Hz), 1.34 (s, 3) and **29**: IR 1681 cm^{-1}; ^{1}H NMR δ 6.15 (t, 1, J = 2 Hz), 6.05 (t, 1, J = 2 Hz), 4.57 (s, 2), 4.39 (t, 2, J = 2 Hz), along with several other products.

Oxidation of 1-*tert*-Butyldimethylsilyloxy-2-butyl-2,3-butadiene (2h). Addition of 25 mL of **1** to 75 mg of **2h** and 2.5 g of $NaHCO_3$ in 2 mL of acetone at -50°C followed by warming to 10°C gave 74 mg (85%) of a 1.1:1 mixture of diastereomers of **5h**: IR 1622 cm^{-1}. Assignments from the spectra of the mixture were tentatively made to ***anti*** **5h**: ^{1}H NMR δ 3.87 (d, 1, J = 12 Hz), 3.83 (d, 1, J = 12 Hz), 3.46 (d, 1, J = 3 Hz), 3.27 (d, 1, J = 3 Hz); ^{13}C NMR δ 84.6, 67.7, 63.7, 48.3 and ***syn*** **5h**: ^{1}H NMR δ 3.91 (d, 1, J = 12 Hz), 3.87 (d, 1, J = 12 Hz), 3.45 (d, 1, J = 3 Hz), 3.28 (d, 1, J = 3 Hz); ^{13}C NMR δ 84.4, 68.2, 63.0, 48.9. Heating a solution of **5h** in refluxing $CHCl_3$ containing $NaHCO_3$ gave a very complex mixture, which was not studied further.

Oxidation of 2-*tert*-Butyldimethylsiloxy-2-methyl-3,4-octadiene (2i). A mixture of 59 mg of **2i** and 15 mL of **1** in acetone was stirred at room temperature for 1 h, after which 2 g of K_2CO_3 was added and the acetone was evaporated. The residue was dissolved in CH_2Cl_2, dried ($MgSO_4$), and concentrated to give 40 mg of a 2:1 mixture of ***anti,anti*** and ***anti,syn*** **5i** as a colorless liquid: IR 1627, 1255, 1165, 1047 cm^{-1}. Small amounts (< 10%) of two isomers of **4i** were also detected by ^{1}H NMR. The ***anti,anti*** isomer of **5i** showed: ^{1}H NMR δ 3.71 (ddd, 1, J = 8, 3, 1 Hz), 3.56 (d, 1, J = 1 Hz), 1.242 (s, 3), 1.238 (s, 3), 0.97 (t, 3, J = 7 Hz), 0.10 (s, 3), 0.08 (s, 3); ^{13}C NMR δ 83.9 (s), 71.8 (s), 65.8 (d), 60.5 (d), 32.5 (t), 26.7 (q), 26.4 (q), 25.7 (q), 18.9 (t), 18.0 (s), 13.7 (q), -2.2 (q), -2.3 (q). The ***anti,syn*** isomer of **5i** showed: ^{1}H NMR δ 3.63 (s, 1), 3.51 (dd, 1, J = 7, 5 Hz), 1.20 (s, 3), 1.19 (s, 3), 0.99 (t, 3, J = 7.5 Hz), 0.09 (s, 3), 0.07 (s, 3); ^{13}C NMR δ 84.3 (s), 71.9 (s), 66.3 (d), 59.6 (d), 31.1 (t), 26.7 (q), 26.2 (q), 25.7 (q), 19.0 (t), 17.9 (s), 13.9 (q), -2.3 (q), -2.4 (q). ^{1}H NMR signals at δ 1.88-1.74 (m), 1.62-1.44 (m), and 0.84 (s) are common to both isomers.

This material was resistant to prolonged refluxing in CCl_4 and was only partially converted after 40 h in toluene at reflux to a complex mixture of products which appears to include unreacted **5i**, **28i**, and **3i**: IR 3450, 1817, 1762, 1717, 1622 cm^{-1}.

6-*tert*-Butyldimethylsiloxy-5,5-dimethyl-3-oxacyclohexanone (13h). To a stirred mixture of 40 mL (10 eq) of **1** in acetone containing 15 g of 4 Å molecular sieves and 1.5 g of $NaHCO_3$ at 0°C was added 90 mg (0.4 mmol) of **12h**. The reaction was stirred at 0°C for 1 h and the mixture was filtered and concentrated. The residue was diluted with ether, dried ($MgSO_4$), and concentrated. Preparative TLC using 1:3 ether/hexane provided 58 mg (56%) of **13h** as a colorless liquid: IR 1742, 1253, 1148, 1110, 862 cm^{-1}; ^{1}H NMR δ 3.91 (AB, 2, Δν = 92 Hz, J = 15 Hz), 3.78 (s), 3.52 (AB, 2, Δν = 83 Hz, J = 12 Hz), 0.92 (s, 3), 0.87 (s, 3), 0.84 (s, 9), 0.02 (s, 3), -0.04 (s, 3); ^{13}C NMR δ 205.3 (s), 81.9 (dm, J = 124 Hz), 75.4 (tm, J = 122 Hz), 73.1 (tm, J = 136 Hz), 42.2 (s), 25.8 (q of heptets, J = 120, 5 Hz), 22.6 (q), 19.0 (q), 18.5 (s), -4.3 (q), -5.3 (q); MS (CI) *m/z* (rel intensity) 201 (15), 171 (6), 159 (4), 117 (100), 89 (6), 75 (33); exact mass 201.094, calcd for $C_9H_{17}O_3Si$ (M-tBu) 201.0970.

Oxidation of 1-*tert*-Butyldimethylsiloxy-2,2-dimethyl-3,4-octadiene (12i). Reaction of 50 mg of 12i and 10 mL (5 eq) of 1 in acetone containing 4 g of 4 Å molecular sieves and 1 g of $NaHCO_3$ gave 56 mg (100%) of a 2.2:1 mixture of ***anti,anti*** and ***anti,syn*** 30i as a viscous colorless liquid: IR 1624, 1256, 1099, 838 cm^{-1}. The major isomer showed: ^1H NMR (C_6D_6) δ 3.70 (d, 1, J = 1.0 Hz), 3.44 (d, 1, J = 9.5 Hz), 3.41 (ddd, 1, J = 8.5, 3, 1.0 Hz), 3.24 (d, 1, J = 9.5 Hz), decoupling at 3.70 gave 3.41 (dd, J = 8.5, 3 Hz); ^{13}C NMR δ 84.2, 69.5, 64.9, 60.4 36.4, 32.7, 25.9, 20.5, 19.8, 19.1, 18.3, 13.7, -5.54, -5.55. The minor isomer showed: ^1H NMR (C_6D_6) δ 3.64 (s, 1), 3.35 (d, 1, J = 10 Hz), 3.33 (dd, 1, J = 7, 5 Hz), 3.21 (d, 1, J = 10 Hz); ^{13}C NMR δ 84.5, 69.3, 65.7, 59.9, 36.5, 31.1, 25.8, 20.4, 20.1, 19.0, 18.3, 13.9, -5.57, -5.61. In the ^1H NMR spectrum, the region between 1.45 and 1.35 δ was not completely resolved, clearly showing only singlets at 1.43, 1.39, 1.38, and 1.36. Heating 30i for 15 h in benzene at reflux gave little reaction.

Oxidation of 1-*tert*-Butyldimethylsiloxy-5-methyl-3,4-hexadiene (12j). A mixture of 46 mg of 12j and 10 mL of 1 gave 48 mg (93%) of a colorless liquid which was predominantly ***anti*** 30j: IR 1635, 1250, 1100, 830 cm^{-1}; ^1H NMR δ 3.85 (dd, 1, J = 7, 4.5 Hz), 3.78 (ddd, 1, J = 12, 6, 5 Hz), 3.75 (ddd, 1, J = 12, 8, 5 Hz), 1.98 (m, 1), 1.76 (ddt, 1, J = 14, 7, 5 Hz), 1.54 (s, 3), 1.48 (s, 3), 0.87 (s, 9), 0.05 (s, 3), 0.04 (s, 3); ^{13}C NMR δ 89.7 (s), 63.3 (s), 59.27 (t), 59.24 (d), 33.5 (t), 25.9 (q), 21.4 (q), 20.3 (q), 18.3 (s), -5.4 (q).

Thermolysis of 30j. A 67-mg sample of 30j was heated in refluxing toluene for 26 h. Evaporation of solvent and column chromatography on silica gel using 4:1 pentane/ether gave 26 mg (39%) of 4-(2-*tert*-butyldimethylsilyloxyethyl)2,2-dimethyl-3-oxetanone (31) and 10 mg (15%) of 32 contaminated with 31. Compound 31 showed: IR 1817, 1256, 1107, 836 cm^{-1}; ^1H NMR δ 5.42 (t, 1, J = 7 Hz), 3.78 (dt, 1, J = 10, 6 Hz), 3.71 (dd, 1, J = 10, 6 Hz), 1.98 (q, 2, J = 6 Hz), 1.46 (s, 3), 1.44 (s, 3), 0.86 (s, 9), 0.027 (s, 3), 0.025 (s, 3); ^{13}C NMR δ 208.9, 102.4, 93.4, 58.1, 35.3, 25.9, 23.31, 23.25, 18.3, -5.4; MS (CI) *m/z* (rel intensity) 259 (6), 243 (5), 201 (32), 173 (66), 159 (65), 143 (33), 131 (52), 127 (16), 115 (39), 101 (41), 75 (100); exact mass 259.172, calcd for $C_{13}H_{27}O_3Si$ 259.1730. 7-*tert*-Butyldimethylsilyloxy-2-methylhept-1-en-3-one (32) showed: IR 3463, 1678, 1630, 1257, 1098, 1060, 940 cm^{-1}; ^1H NMR δ 5.97 (br s, 1), 5.88 (q, 1, J = 1.5 Hz), 4.96 (dd, 1, J = 9, 3 Hz), 3.78 (m, 2), 3.44 (br s, 1), 2.00 (m, 1), 1.92 (dd, 3, J = 1.5, 1 Hz), 1.56 (m, 1), 0.88 (s, 9), 0.05 (s, 3), 0.04 (s, 3).

Oxidation of 1-*tert*-Butyldimethylsilyloxy-3,4-octadiene (12k). To a stirred mixture of 1 g of $NaHCO_3$, 4 g of 4 Å molecular sieves and 10 mL of 1 at -40°C was added 40 mg of 12k. After gradual warming to 20°C over 6 h, concentration, drying of an ether solution (K_2CO_3) and concentration gave crude 30k: IR 1626 cm^{-1}. Heating to reflux in $CDCl_3$ containing solid $NaHCO_3$ for 20 h gave a product containing a 2:1 mixture of ***trans*** and ***cis*** 13k as a major component. Isolation by TLC gave 5 mg (11%) of 13k identical to that prepared above from **12e**.

Oxidation of 1-*tert*-Butyldimethylsiloxy-3,4-pentadiene (12*l*). A mixture of 17 mg of 12*l* and 1 g of anhydrous MgSO$_4$ in 6 mL of 1 gave 22 mg of a yellow liquid which consisted of *anti* 30*l*, *syn* 30*l*, and 33 in the proportions of 3.4:1:1.4. Characteristic ^{1}H NMR signals at δ 3.47 (dd, 1, J = 3, 1 Hz) and 3.31 (d, 1, J = 3 Hz) were assigned to *anti* 30l, and those at δ 3.53 (d, 1, J = 3 Hz) and 3.36 (d, 1, J = 3 Hz) to *syn* 30l. The presence of 33 was indicated by signals at δ 4.52 (ABq of d, J = 19, 5 Hz), 4.41 (m), 3.10 (br d), and 2.96 (br t).

Thermolysis of 30*l*. A sample of 30*l* obtained from 17 mg of 12*l* was heated for 4 h in refluxing CCl$_4$ containing 1 g of MgSO$_4$. Evaporation of solvent and column chromatography on silica gel using 2:1 ether/pentane gave 9 mg (46%) of 13*l* as a colorless liquid: IR 1740 cm^{-1}; ^{1}H NMR δ 4.26 (dd, 1, J = 9.5, 6 Hz), 4.14 (d, 1, J = 15 Hz), 4.02 (dt, 1, J = 12, 5 Hz), 3.94 (d, 1, J = 15 Hz), 3.79 (m, 1), 2.28 (m, 1), 2.08 (m, 1), 0.88 (s, 9), 0.11 (s, 3), 0.05 (s, 3); ^{13}C NMR δ 205.0 (s), 73.9 (t), 73.7 (d), 64.9 (t), 36.5 (t), 25.7 (q), 18.3 (s), -4.7 (q), -5.4 (q).

Oxidation of 1-*tert*-Butyldimethylsilyloxy-6-methyl-4,5-heptadiene (17d). Reaction of 72 mg of 17d and 3 g of K$_2$CO$_3$ in 10 mL of acetone with 19 mL of 1 gave 74 mg (91%) of a 9:1 mixture of *anti* and *syn* 34d. The major isomer showed: ^{1}H NMR δ 3.77 (dd, 1, J = 6, 3 Hz), 3.7-3.6 (m, 2), 1.9-1.8 (m, 1), 1.8-1.7 (m, 1), 1.66-1.56 (m, 2), 1.54 (s, 3), 1.48 (s, 3), 0.87 (s, 9), 0.03 (s, 6); The *syn* isomer was assigned on the basis of peaks at 1.53 (s) and 1.47 (s); the other signals were obscured. Heating this mixture for 15 h in tetrachloroethylene containing K$_2$CO$_3$ gave a very complex mixture of products containing 35d as a major component: IR 1817 cm^{-1}; ^{1}H NMR δ 5.32 (t, J = 7 Hz).

Oxidation of 2-*tert*-Butyldimethylsiloxy-2,7-dimethyl-5,6-octadiene (17e). Reaction of 43 mg of 17e and 16 mL of 1 gave 47 mg (98%) of a 9:1 mixture of *anti* and *syn* 34e as a colorless liquid: IR 1635, 1252, 1212, 1155, 1040 cm^{-1}. The major isomer showed: ^{1}H NMR δ 3.73 (dd, 1, J = 6, 5.5 Hz), 1.81 (m, 2), 1.53 (s, 3), 1.50 (m, 2), 1.49 (s, 3), 1.19 (s, 6), 0.82 (s, 9), 0.04 (s, 6); ^{13}C NMR δ 89.5 (s), 72.6 (s), 63.3 (s), 61.9 (d), 40.0 (t), 29.68 (q), 29.66 (q), 25.76 (q), 24.8 (t), 21.6 (q), 20.2 (q), 18.1 (s), -2.1 (q). The minor isomer showed: ^{1}H NMR (partial) δ 3.54 (dd, 1, J = 7, 6 Hz), 1.52 (s, 3), 1.46 (s, 3); ^{13}C NMR (partial) δ 90.1, 72.9, 61.0, 40.4, 29.8, 29.6, 25.81, 24.2, 21.8, 20.0. A sample of 34e was heated in toluene at reflux for 44 h to give crude oxetanone 35e as a colorless liquid: ^{1}H NMR δ 5.25 (t, 1, J = 7 Hz), 1.88 (m, 2), 1.51 (m, 2), 1.45 (s, 3), 1.43 (s, 3), 1.180 (s, 3), 1.177 (s, 3), 0.81 (s, 9), 0.039 (s, 3), 0.036 (s, 3); ^{13}C NMR δ 208.9 (s), 101.9 (s), 96.8 (d), 72.7 (s), 39.4 (t), 29.7 (q), 29.6 (q), 27.1 (t), 25.8 (q), 23.15 (q), 23.11 (q), 18.0 (s), -2.1 (q).

Oxidation of 1-*tert*-Butyldimethylsiloxy-7-methyl-5,6-octadiene (20d). Reaction of 38 mg of 20d and 10 mL of 1 gave 42 mg (98%) of a 9:1 mixture of *anti* and *syn* 36d as a colorless liquid: IR 1637, 1256, 1101 cm^{-1}. The major isomer showed: ^{1}H NMR δ 3.72 (dd, 1, J = 6, 5 Hz), 3.59 (t, 2, J = 6 Hz), 1.82-1.62 (m, 2), 1.58-1.44 (m, 4), 1.53 (s, 3), 1.47 (s, 3), 0.86 (s, 9), 0.01 (s, 6); ^{13}C NMR δ 89.3 (s), 63.3 (s), 62.7 (t), 61.6 (d), 32.4 (t), 29.7 (t), 25.9 (q), 21.7 (t), 21.5 (q), 20.2 (q), 18.3 (s), 5.4 (q). The minor isomer showed: ^{1}H NMR (partial) δ 3.55 (dd, 1, J = 6.5, 6 Hz), 1.52 (s, 3), 1.46 (s, 3), 0.88 (s, 9), 0.06 (s, 6); ^{13}C NMR δ 89.9 (s), 64.3 (s), 62.7 (t), 60.6 (t), 32.3 (t), 28.7 (t), 25.6 (q), 22.1 (t), 21.7 (q), 20.0 (q), 17.9 (s), -3.6 (q).

Thermolysis of 36d. A 104-mg sample of **36d** was heated in toluene at reflux for 40 h. Evaporation of the solvent gave predominantly **37d** with 6% of **38**. 4-(4-*tert*-Butyldimethylsilyloxybutyl)-2,2-dimethyl-3-oxetanone (**37d**) was purified by column chromatography on silica gel using 3:1 pentane/ether: IR 1817, 1256, 1101 cm^{-1}; ^{1}H NMR δ 5.28 (t, 1, J = 7 Hz), 3.59 (t, 2, J = 6 Hz), 1.81 (q, 2, J = 7 Hz), 1.52 (m, 2), 1.46 (s, 3), 1.43 (s, 3), 1.28 (m, 2), 0.86 (s, 9), 0.02 (s, 6); ^{13}C NMR δ 208.9 (s), 102.1 (s), 96.5 (d), 67.7 (t), 32.4 (t), 31.8 (t), 25.9 (q), 23.14 (q), 23.11 (q), 21.2 (t), 18.3 (s), -5.3 (q); MS(CI) *m/z* (rel intensity) 287 (18), 230 (11), 229 (66), 215 (24), 171 (30), 157 (49), 143 (21), 129 (29), 75 (100); exact mass 287.203, calcd for $C_{15}H_{31}O_3Si$ 287.2043. 8-*tert*-Butyldimethylsilyloxy-2-methyloct-1-en-3-one (**38**) showed: IR 3464, 1677, 1630, 1256, 1103, 1059, 836, 776 cm^{-1}; ^{1}H NMR δ 5.88 (br s, 1), 5.87 (q, 1, J = 1.5 Hz), 4.78 (dd, 1, J = 7, 3 Hz), 3.56 (t, 2, J = 6 Hz), 3.46 (br s, 1), 1.91 (dd, 3, J = 1.5, 1 Hz), 1.77 (m, 1), 1.56-1.40 (m, 4), 1.40-1.32 (m, 1), 0.85 (s, 9), 0.00 (s, 6); ^{13}C NMR δ 203.6 (s), 141.4 (s), 126.2 (t), 72.3 (d), 62.8 (t), 36.2 (t), 32.5 (t), 25.9 (q), 21.3 (t), 18.3 (s), 17.8 (q), -5.3 (q); MS(CI) *m/z* (rel intensity) 287 (20), 229 (66), 155 (23), 137 (28), 109 (37), 85 (96), 75 (100); exact mass 287.206, calcd for $C_{15}H_{31}O_3Si$ 287.2043.

Oxidation of 1-*tert*-Butyldimethylsiloxy-5,6-heptadiene (20e). A. To a mixture of 51 mg of **20e** and 2.5 g of $NaHCO_3$ in 3 mL of acetone at -78°C was added 18 mL of **1**. After warming to room temperature and stirring for 5 h, the solvent was removed to give a mixture of **20e** and **39e**. Preparative TLC using 1:4 pentane/ether gave 26 mg (45%) of 7-*tert*-butyldimethylsilyloxyl-1,3-dihydroxy-2-heptanone (**39e**) as an oil: IR 3400, 1724, 1256, 1099 cm^{-1}; ^{1}H NMR δ 4.48 (ddd, 1, J = 19.5, 5, 1 Hz), 4.38 (dd, 1, J = 19.5, 5 Hz), 4.29 (ddd, 1, J = 8, 5, 4 Hz), 3.61 (t, 2, J = 6 Hz), 3.05 (d, 1, J = 5 Hz), 2.88 (t, 1, J = 5 Hz), 1.82 (m, 1), 1.65-1.42 (m, 3), 0.87 (s, 9), 0.03 (s, 6). ^{13}C NMR δ 212.1, 75.2, 65.8, 63.1, 34.0, 32.3, 26.2, 21.5, 18.6, -5.03; MS (CI) *m/z* (rel intensity) 277 (2), 201 (12), 183 (14), 171 (7), 127 (16), 117 (17), 185 (55), 75 (100); exact mass 277.185, calcd for $C_{13}H_{29}O_4Si$ 277.1835.

B. Reaction of 45 mg of **20e** and 1 g of anhydrous $MgSO_4$ with 20 mL of **1** gave 45 mg of a colorless liquid which consisted of *anti* **36e**, *syn* **36e** and **39e** in a ratio of 3:1:1: IR 1723, 1619 cm^{-1}. *Anti* **36e** showed: ^{1}H NMR (partial) δ 3.75 (td, 1, J = 6, 1 Hz), 3.46 (dd, 1, J = 3, 1 Hz), 3.29 (d, 1, J = 3 Hz); ^{13}C NMR δ 82.2 (s), 62.6 (t), 60.3 (d), 47.8 (t), 32.3 (t), 29.7 (t), 25.9 (q), 21.6 (t), 18.3 (s), -5.4 (q). *Syn* **36e** showed: ^{1}H NMR (partial) 3.51 (d, 1, J = 3 Hz), 3.34 (d, 1, J = 3 Hz); ^{13}C NMR (partial) δ 82.5 (s), 62.8 (t), 49.0 (t). Overlapping ^{1}H signals at δ 3.59, 1.80, and 1.52 are common to *anti* **36e**, *syn* **36e**, and **39e**.

Thermolysis of 36e. A sample of **36e** obtained from 34 mg of **20e** was heated for 4 h in CCl$_4$ containing 1 g of anhydrous MgSO$_4$. Evaporation of solvent and column chromatography on silica gel using 5:1 pentane/ether gave 12 mg (31%) of 2-(2-*tert*-butyldimethylsilyloxy-1-oxoethyl)tetrahydropyran (**21e**) as a yellow liquid: IR 1730 cm^{-1}; ^{1}H NMR δ 4.49 (AB, 2, Δν = 19 Hz, J = 19 Hz,), 4.01 (m, 1), 3.97 (dd, 1, J = 11, 2.5 Hz), 3.42 (td, 1, J = 11.5, 2 Hz), 1.93 (m, 1), 1.88 (m, 1), 1.60-1.48 (m, 3), 1.45-1.35 (m, 1), 0.90 (s, 9), 0.07 (s, 6); ^{13}C NMR δ 208.5 (s), 81.6 (d), 68.3 (t), 67.0 (t), 28.4 (t), 25.8 (q), 5.5 (t), 23.0 (t), 18.4 (s), -5.5 (q). These NMR data are nearly identical with those of the corresponding alcohol **21c**. The presence of **20e**, **39e**, and several other compounds was indicated in the ^{1}H NMR of the crude product.

Oxidation of 1-*tert*-Butyldimethylsilyloxy-5-methyl-5,6-heptadiene (20f). Reaction of 26 mg of **20f** with 10 mL (10 equiv) of **1** gave 27 mg of a 2:1 mixture of stereoisomers of **36f**. The major isomer showed: ^{1}H NMR δ 3.577 (t, 2, J = 6 Hz), 3.49 (d, 1, J = 3 Hz), 3.32 (d, 1, J = 3 Hz), 1.53 (s, 3). The minor isomer showed: ^{1}H NMR δ 3.583 (t, 2, J = 6 Hz), 3.44 (d, 1, J = 3 Hz), 3.28 (d, 1, J = 3 Hz), 1.48 (s, 3). Overlapping signals at δ 1.7-1.9 (m), 1.3-1.6 (m), 0.87 (s) and 0.02 (s) are common to both isomers. Variable amounts of **37f**, **39f**, and **40** were observed spectroscopically as by-products by ^{1}H NMR in different reactions.

Heating this mixture for 4 h in refluxing CCl$_4$ gave a mixture of **37f**: IR 1818 cm^{-1}; ^{1}H NMR δ 5.13, (ABq, J = 15 Hz), **39f**: IR 1720 cm^{-1}; ^{1}H NMR δ 4.61 (ABq of d, J = 20, 5 Hz), and **40**: IR 1683 cm^{-1}; ^{1}H NMR δ 5.91 (br s), 5.80 (t, J = 1.4 Hz), 4.54 (d, J = 5 Hz), 2.94 (t, J = 5 Hz), tentatively assigned on the basis of these data.

Oxidation of 1-*tert*-Butyldimethylsiloxy-8-methyl-6,7-nonadiene (22c). A mixture of 34 mg of **22c** and 30 mL of **1** gave 40 mg (100%) of a 9:1 mixture of *anti* and *syn* **26c** as a colorless liquid: IR 1637, 1255, 1101, 1024, 1090, 836 cm^{-1}. The major isomer showed: ^{1}H NMR δ 3.72 (dd, 1, J - 6, 5 Hz), 3.58 (t, 2, J = 6.5 Hz), 1.80-1.71 (m, 1), 1.70-1.62 (m, 1), 1.53 (s, 3), 1.47 (s, 3), 1.52-1.35 (m, 6), 0.86 (s, 9), 0.01 (s, 6); ^{13}C NMR δ 89.4, 63.3, 62.9, 61.6, 32.6, 29.9, 25.9, 25.6, 25.1, 21.5, 20.2, 18.3, -5.3. Characteristic ^{1}H NMR signals at δ 3.57 (t, J = 6 Hz), 3.54 (dd, J = 6.5, 6 Hz), 1.52 (s), and 1.46 (s) were assigned to the minor isomer.

Thermolysis of Spirodioxide 26c. A 40-mg sample of **26c** was heated in refluxing toluene for 4 h. Purification by column chromatography on silica gel using 5:1 hexane/ether gave 18 mg (46%) of 2,2-dimethyl-4-(5-*tert*-butyldimethylsilyloxypentyl)-3-oxetanone (**24c**) as a colorless liquid: IR 1817, 1256, 1101, 836, 775 cm^{-1}; ^{1}H NMR δ 5.27 (t, 1, J = 7 Hz), 3.57 (t, 2, J = 6.5 Hz), 1.79 (td, 2, J = 8, 7 Hz), 1.50 (tt, 2, J = 7, 6.5 Hz), 1.45 (s, 3), 1.44 (m, 2), 1.43 (s, 3), 1.36 (m, 2), 0.86 (s, 9), 0.02 (2, 6); ^{13}C NMR δ 208.9 (s), 102.0 (s), 96.5 (d), 63.0 (t), 32.6 (t), 32.0 (t), 26.0 (q, 3), 25.5 (t), 24.5 (t), 23.1 (q, 2), 18.3 (s), 5.3 (q, 2); MS(CI) *m/z* (rel intensity) 243 (13), 229 (4), 215 (2), 185 (9), 173 (9), 171 (42), 131 (13), 75 (100); exact mass 243.142, calcd for $C_{12}H_{23}O_3Si$ (M-tBu) 243.1417.

REFERENCES

1. Crandall, J. K.; Conover, W. W.; Komin, J. B.; Machleder, W. H. *J. Org. Chem.* **1974**, *39*, 1723. For reviews of allene oxide chemistry, see: Stang, P. J. *The Chemistry of Functional Groups, Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulfur Analogs*; Patai, S., Ed.; Wiley: New York, 1980; pp 859-879; L'Abbe, G. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 276.
2. For reviews on dioxirane oxidations, see: Curci, R. *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1988; Vol. 2, Chapter 1. Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205.
3. Crandall, J. K.; Batal, D. J.; Sebesta, D. P.; Lin, F. *J. Org. Chem.* **1991**, *56*, 1153.
4. For a preliminary communication, see: Crandall, J. K.; Batal, D. J. *Tetrahedron Lett.* **1988**, *29*, 4791.
5. Crandall, J. K.; Rambo, E. *J. Org. Chem.* **1990**, *55*, 5929.
6. Bertrand, M.; Dulcere, J. P.; Gil, G.; Grimaldi, J.; Sylvestre-Panthet, P. *Tetrahedron Lett.* **1976**, 1507 and 3305. Bertrand, M.; Dulcere, J. P.; Gil, G. *Tetrahedron Lett.* **1977**, 3807.
7. Conover, W. W. Ph.D. Thesis, Indiana University, Bloomington, 1973.
8. Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, *45*, 5703.
9. Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847; Cassidei, L.; Fiorentino, M.; Mello, R.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1987**, *52*, 699.
10. Laslo, P.; Musher, J. I. *Bull. Soc. Chim. Fr.* **1964**, 2558.
11. Cicala, G.; Curci, R.; Fiorentino, M.; Laricchiuta, O. *J. Org. Chem.* **1982**, *47*, 2670. Murray, R. W.; Zabrowski, D. L.; Noorman, A. E.; Beck, K. R.; *Tetrahedron Lett.* **1988**, 6501. Curci, R.; Fiorentino, N.; Serco, N. R. *J. Chem. Soc., Chem. Commun.* **1984**, 156.
12. Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1988**, *53*, 3890.
13. Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734 and 738. March, J. *Advanced Organic Chemistry*; 3rd Ed.; Wiley: New York, 1985; p 187. Carey, F. A.; Sundberg, R. J. *Advanced Organic Chem. Part A Structure and Mechanisms*; 3rd Ed.; Plenum: New York, 1990; pp 165-167.
14. Berti, G. *Top. Stereochem.* **1973**, *7*, 93. Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323.
15. Cowie, J. S.; Landor, P. D.; Landor, S. R. *J. Chem. Soc., Perkin I* **1973**, 20.
16. Hoff, S.; Brandsma, L.; Arens, J. F. *Rec. Trav. Chim. Pays-Bas* **1968**, *87*, 159.
17. Sydnes, L. K.; Skattebol, L. *Acta Chem. Scand.* **1978**, *B32*, 632.
18. Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 916.
19. Crandall, J. K.; Tindell, G. L.; Manmade, A. *Tetrahedron Lett.* **1982**, *23*, 3769.
20. Bly, R. S.; Koock, S. U. *J. Am. Chem. Soc.* **1969**, *91*, 3292.
21. Macdonald, T. L.; Reagan, D. R. *J. Org. Chem.* **1980**, *45*, 4740.
22. Santelli, M.; Bertrand, M. *Bull. Chem. Soc. Fr.* **1973**, 2326.
23. Apparu, M.; Crandall, J. K. *J. Org. Chem.* **1984**, *49*, 2125.
24. Ragonnet, B.; Santelli, M.; Bertrand, M. *Helv. Chim. Acta* **1974**, *57*, 557.
25. Marbet, R.; Saucy, G. *Helv. Chim. Acta* **1967** , *50*, 1158.
26. Crandall, J. K.; Mualla, M. *Tetrahedron Lett.* **1986**, *27*, 2243.
27. Johnston, M. I.; Kwass, J. A.; Beal, R. B.; Snider, B. B. *J. Org. Chem.* **1987**, *52*, 5419.
28. Brandsma, L.; Verkruijsse, H. D. *Synthesis of Allenes, Acetylenes and Cumulenes*; Elsevier: New York, 1981; p 30.
29. Clinet, J. C.; Linstrumelle, G. *Synthesis* **1981**, 875.