Oxidative Cyclization of δ,ε- and ε,ζ-Unsaturated Enol Silyl Ethers and Unsaturated Siloxycyclopropanes

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Oxidative cyclization of δ,ε- and ε,ζ-unsaturated enol silyl ethers **4a** and **4b** with cupric triflate and cuprous oxide or ceric ammonium nitrate and sodium bicarbonate in acetonitrile provides the tricyclic ketones **5a** and **5b** stereoselectively. These cyclizations proceed by oxidation of **4** to the cation radical **24** followed by cyclization of **24** to cation radical **27**. This cation radical undergoes a second cyclization to give cation radical **30**, which loses the silyl group, undergoes a second oxidation, and loses a proton to give **5**. The stereochemistry of the cycloadduct is controlled by the stereochemistry of the enol ether. The *Z*-enol methyl ether (*Z*)-**65** leads mainly to **5a** while the *E*-enol methyl ether (*E*)-**65** leads mainly to **6a**. The oxidative cyclizations of **7**, **13**, **21**, and **43** are also described. Oxidation of α-allyl silyl enol ethers **34a** and **34b** leads mainly to oxidation without cyclization to give the α,β-unsaturated ketones **36a** and **36b**. Oxidative cyclizations of alkynyl silyl enol ethers **56** and **60** lead to **15** and **64**, respectively. Oxidation of siloxycyclopropane **74** with $Cu(BF_4)_2$ generates cation radical **75**, which cyclizes to **76**, which is oxidized to give 21% of cyclopentane **77**. This suggests that cation radicals are intermediates in the oxidative dimerization of siloxycyclopropanes.

Introduction

We recently reported oxidative free-radical cyclizations that are initiated by oxidation of β-dicarbonyl compounds with $Mn(OAc)_3 \cdot 2H_2O$.[1] The scope of these reactions would be extended if they could be initiated by oxidation of a monocarbonyl compound. Unfortunately, oxidative cyclizations of ε,ζ-unsaturated ketones will probably not be practical, since intermolecular oxidative additions of ketones to alkenes are successful[2] only when a large excess of ketone is used to preclude further oxidation of the product. Oxidative cyclization of δ,ε- and ε,ζ-unsaturated enolates or enol ethers did appear to be viable since the oxidative coupling of enolates or enol ethers with copper(II)[3-5] cerium(IV),[6,7] Fe(III),[8a] Pb(IV),[8b] or Ag(I)[9] can be carried out without further oxidation of the product diketones. We expected that conditions could be developed in which either an enol radical or a cation radical, prepared by the oxidation of an enol ether, would add intramolecularly to an alkene more rapidly than it would add intermolecularly to a second enol ether.

We report here that oxidative cyclizations of δ,ε- and ε,ζ-unsaturated enol silyl ethers can be carried out with either copper(II) or cerium(IV).[10] Moeller has recently shown that similar cyclizations can be carried out by anodic oxidation.[11] Both of these oxidative cyclizations are mechanistically distinct from the palladium(II)-mediated cyclizations of unsaturated enol silyl ethers studied by Saegusa[12] and Kende[13] that appear to proceed by addition of the nucleophilic silyl enol ether to the electrophilic palladium-alkene complex.

Results and Discussion

Oxidative Cyclization of Silyl Enol Ethers of Unsaturated Aromatic Ketones. We chose phenyl ketone **1a** for initial studies since only one regioisomeric enolate or enol ether can be formed and the phenyl group might act as a trap for the monocyclic intermediate formed from the initial cyclization. The chain length was chosen since the cyclization of 5-hexenyl radicals to give cyclopentanemethyl radicals is faster than the formation of smaller or larger rings. Treatment of (*Z*)-6-nonenal with PhMgBr followed by Jones' oxidation of the resulting alcohol gives **1a**. Reaction of lithium enolate **2a** in THF at −78 °C with a solution of $Cu(OTf)_2$ and Cu_2O in *i*-PrCN as described by Kobayashi[4] for the oxidative dimerization of enolates gives only the dimeric 1,4-diketone. Not surprisingly, intramolecular coupling of the enol radical with

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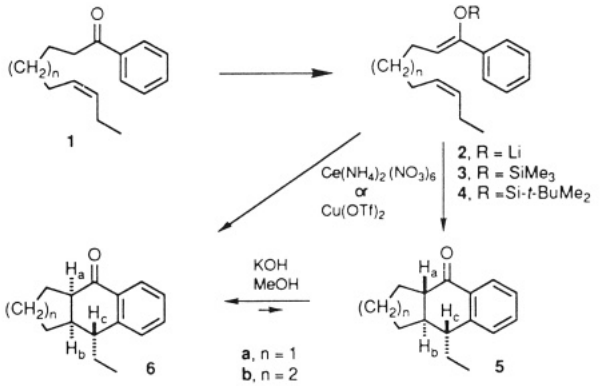
the alkene cannot compete with intermolecular coupling with the very reactive enolate. We therefore turned our attention to oxidative cyclization of unsaturated enol ethers.



Our initial success was achieved in the oxidative cyclization of trimethylsilyl enol ether **3a**, which gives 10% of a 20:1 mixture of **5a** and **6a**. The major product is ketone **1a**, which indicates that trimethylsilyl enol ethers are not stable to the reaction conditions. We therefore turned our attention to more hydrolytically stable silyl enol ethers. Treatment of ketone **1a** with Et_3N and *tert*-butyldimethylsilyl triflate (TBDMSOTf) in CH_2Cl_2 gives 90% of a 5:1 mixture of (*Z*)-**4a** and (*E*)-**4a**.[14] Alternatively, treatment of lithium enolate **2a** with TBDMSOTf affords 88% of pure (*Z*)-**4a**.[15,16] The stereochemistry of the enol ether double bond was assigned based on chemical shifts in the ^1H and ^{13}C NMR spectra. The vinyl hydrogen (OC=C*H*) absorbs downfield (δ 5.11 vs 5.08), C_2 (*C*=CO) absorbs downfield (δ 111.7 vs 111.1), and the silylmethyl carbons absorb upfield (δ −4.0 vs +0.5) in the *Z*-isomer.[16]

Reaction of (*Z*)-**4a** with excess Cu_2O and $Cu(OTf)_2$ at 0 °C in CH_3CN, as described by Kobayashi for the oxidative dimerization of trimethylsilyl enol ethers,[4] affords 90% of a 20:1 mixture of tricyclic ketones **5a** and **6a**. Similarly, reaction of **4a** with 2 equiv of ceric ammonium nitrate (CAN) and excess $NaHCO_3$ at rt in CH_3CN, as described by Baciocchi[6] for the oxidative dimerization of trimethyl silyl enol ethers, provides 88% of a 20:1 mixture of **5a** and **6a**. Oxidation of **4a** with 2 equiv of $Cu(BF_4)_2$ and excess of Cu_2O at rt in CH_3CN gives 62% of a 20:1 mixture of **5a** and **6a**. Other oxidants are less successful in carrying out these transformations. Oxidation of (*Z*)-**7** (vide infra) with 2 equiv of tris(*p*-bromophenyl)aminium hexachloroantimonate[17] and excess Na_2CO_3 gives 41% of a 2.5:1 mixture of **8** and **9**. This procedure is of mechanistic interest since it is known to be an effective way of generating cation radicals. However, it is of limited synthetic interest since 2 equiv of the aminium cation are consumed and purification of the product is difficult. No tricyclic products are obtained from treatment of (*Z*)-**4a** with

Figure 1. Calculated conformations of **5** and **6**.

$TiCl_4$,[18] $Fe(ClO_4)_3$,[19] $Mn(OAc)_3$, or PhIO and HBF_4.[20]

The stereochemistry of the major isomer **5a** was assigned based on the coupling constants $J_{Hb,Hc}$ = 10.7 Hz and $J_{Ha,Hb}$ = 13.3 Hz, which require that H_a, H_b, and H_c are all axial (see Figure 1). Equilibration of **5a** with KOH in MeOH gives a 7.7:1 mixture of **6a** and **5a**, thereby establishing the stereochemistry of the minor product **6a** as shown. The equilibrium mixture corresponds closely to that predicted by MM2 calculations,[21] which suggest that **6a** is more stable than **5a** by 1.3 kcal/mol and is similar to the 2:1 cis–trans equilibrium mixture observed in the parent system lacking the ethyl group.[22]

The trans-fused isomer **5a** is locked in a rigid conformation. The only question is the conformation of the ethyl group. MM2 calculations suggest that the methyl group is antiperiplanar to the ring hydrogen H_c to avoid interactions with the outside rings. In this conformation the calculated coupling constants between H_c and the CH_2 group are 4.3 and 2.6 Hz. This prediction is confirmed by the unusually small coupling of 3.8 Hz observed between H_c and the CH_2 group, and the absorption of methyl group of **5a** upfield at δ 8.1 in the ^{13}C NMR spectra due to two gauche butane interactions. The methyl group of **6a**, which has only one gauche butane interaction, absorbs at δ 12.3.

The cis-fused isomer **6a** is calculated to be more stable in the conformation with an axial ethyl group to avoid steric interactions between the ethyl group and outside rings. The observed smaller couplings $J_{Hb,Hc}$ = 8 Hz and $J_{Ha,Hb}$ = 7 Hz are expected for the cis conformer since there are no axial–axial couplings.

Oxidative cyclization of **4b** was examined to determine the suitability of this approach for forming cyclohexanes. Phenyl ketone **1b** was prepared analogously from (*Z*)-7-decenal. Reaction of enolate **2b** with TBDMSOTf affords silyl enol ether (*Z*)-**4b**. Oxidative cyclization of (*Z*)-**4b** with $Cu(OTf)_2$ as described above affords 87% of a 20:1 mixture of tricyclic ketones **5b** and **6b**. Oxidation of (*Z*)-**4b** with CAN is less successful, providing a complex mixture containing 42% of a 4.3:1 mixture of **5b** and **6b**, and 3% of the α-nitrooxy unsaturated acyclic ketone.

The stereochemistry of **5b** was assigned based on $J_{Hb,Hc}$ = 10.4 Hz indicating that H_b and H_c are axial. $J_{Ha,Hb}$ cannot be determined since the ring fusion hydrogens absorb as part of a three hydrogen multiplet. Equilibration of **5b** with KOH in MeOH provides a 1:2.5 mixture of **5b**

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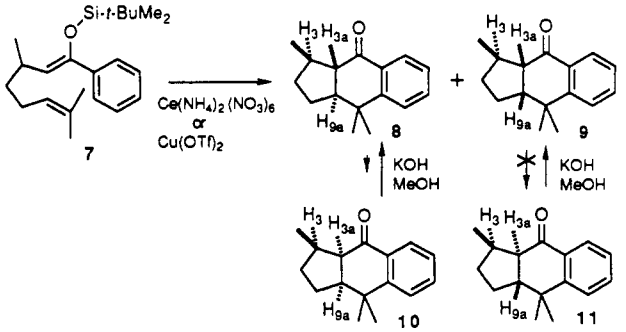
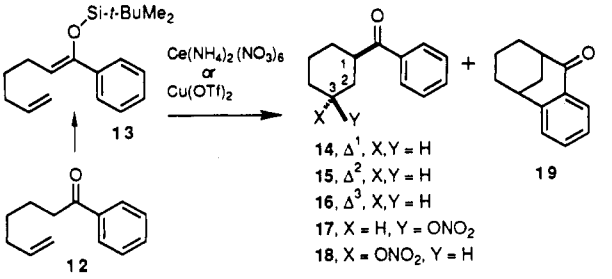
and **6b**. MM2 calculations[21] suggest that the cis-fused isomer **6b** should be more stable than the trans-fused isomer **5b** by 1.3 kcal/mol. As discussed above, the methyl group of **5b** is calculated to be antiperiplanar to H_c resulting in the observed small coupling constants between H_{10} and the adjacent methylene group of 3.6 Hz and the upfield shift of the methyl carbon to δ 7.60 in the ^{13}C NMR spectrum. Isomer **6b** is calculated to be more stable in the configuration with an axial ethyl group to avoid steric interactions between the ethyl group and the outside rings.

Silyl enol ether **7** was examined to determine the effect of a methyl substituent on the stereochemistry of the products. The ketone precursor was prepared by addition of PhMgBr to citronellal followed by oxidation of the alcohol with Jones' reagent. Treatment of the ketone with TBDMSOTf[15] gives an 8:1 mixture of (*Z*)-**7** and (*E*)-**7**. Oxidative cyclization of (*Z*)-**7** with $Cu(OTf)_2$ gives 90% of a 3.2:1 mixture of tricyclic ketones **8** and **9** in 90% yield and while CAN affords 73% of a 3:1 mixture of **8** and **9**.



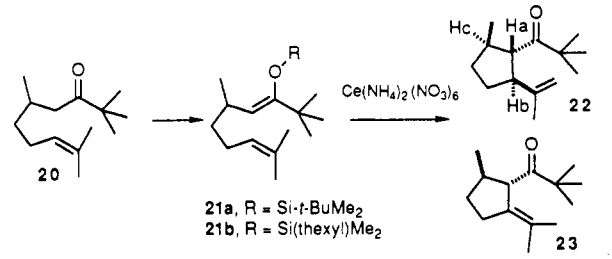
The stereochemical assignment of **8** and **9** follows from the coupling constants and absence of significant epimerization on treatment of either isomer with KOH in MeOH. Large coupling constants $J_{H3a,H9a}$ = 13.6 Hz and $J_{H3,H3a}$ = 8.7 Hz for **8** indicate that the ring fusion is trans. These coupling constants are close to the coupling constants of 12.6 and 10.6 Hz calculated by MM2 for **8**. Equilibration of **8** with KOH in MeOH affords a >9:1 mixture of **8** and **10**, which is consistent with MM2 calculations that **8** is 0.7 kcal/mol more stable than **10**. The stereochemistry of **9** was assigned on the basis of $J_{H3a,H9a}$ = 8.2 Hz and $J_{H3,H3a}$ = 5.5 Hz, which indicate that the ring fusion is cis. These coupling constants are close to the 7.8 and 5.2 Hz values calculated for **9**. Equilibration of **9** with KOH in MeOH gives no **11**, which is consistent with MM2 calculations that **11** is 2.76 kcal/mol less stable than **9**.

More complex mixtures are obtained from oxidation of substrates with terminal double bonds. Ketone **12** was prepared by treatment of 6-heptenonitrile with PhMgBr.[23] Reaction of **12** with Et_3N and TBDMSOTf in CH_2Cl_2 gives an 8:1 mixture of (*Z*)-**13** and (*E*)-**13**. Oxidative cyclization of (*Z*)-**13** with $Cu(OTf)_2$ gives 5% of ketone **12**, 9% of **16**,[24] 2% of **14**,[24] and 7% of tricyclic ketone **19**.[25] Oxidation of (*Z*)-**13** with CAN affords 1% of ketone **12**, 29% of **16**,[24] 1% of **15**,[26] 2% of tricyclic ketone **19**,[25] 16% of *cis*-nitrooxy ketone **17**, and 30% of *trans*-nitrooxy ketone **18**. Oxidative cyclization of (*Z*)-**13** proceeds efficiently, especially with CAN. However, complex mixtures of products **14**–**18** are obtained since cyclization of the monocyclic intermediate to give **19** is slow.



Oxidative Cyclization of Silyl Enol Ethers of Unsaturated Aliphatic Ketones. The phenyl group clearly plays a key role in the cyclization of **4** and **7**. The monocyclic intermediates resulting from 5-*exo* or 6-*exo* cyclization cyclize to the benzene ring to give tricyclic products in excellent yield. Complex mixtures of products are obtained from **13** in which the phenyl group is not well-positioned to react with the intermediate resulting from 6-*endo* cyclization. The phenyl group could also play a crucial role in reducing the oxidation potential of the silyl enol ether. We therefore set out to examine the oxidative cyclization of silyl enol ethers derived from aliphatic ketones. *tert*-Butyl ketones were chosen for initial study to preclude the formation of regioisomeric enol ethers.

Treatment of citronellal with *t*-BuLi and Jones' oxidation of the resulting alcohol affords the *tert*-butyl ketone **20**, which is treated with Et_3N and TBDMSOTf to give a 10:1 mixture of (*Z*)-**21a** and (*E*)-**21a**. Reaction of this mixture with 2 equiv of CAN and excess $NaHCO_3$ in CH_3CN gives 20% of hydrolysis product **20**, 20% of cyclic ketone **22**, and 2% of cyclic ketone **23**. Since hydrolysis of the silyl enol ether to give **20** is a major side reaction, the more hindered dimethylthexylsilyl enol ether was investigated. Oxidation of **21b**[27] with 2 equiv of CAN and excess $NaHCO_3$ provides 42% of cyclic ketone **22**. Unfortunately, the oxidative cyclization of aliphatic silyl enol ethers is not general. No cyclic products were obtained from oxidation of **21a** or **21b** with $Cu(OTf)_2$ or from oxidation of aliphatic silyl enol ethers analogous to **1** or **13** with less nucleophilic monosubstituted or 1,2-disubstituted double bonds.



The Mechanism of Oxidative Cyclization of Unsaturated Enol Ethers. The tandem oxidative cyclizations of **4a**, **4b**, and **7** involve six discreet steps: two one-electron oxidations, two cyclizations, loss of a proton, and loss of the silyl group. The first step is probably the one-electron oxidation of **4** to cation radical **24**. Some information about the order of the remaining steps can be inferred from the products isolated. Loss of the silyl group from cation radical **24** would give radical **25**. One-electron oxidation of radical **25** would give enol cation **26**. Each of these intermediates **24**–**26** could cyclize to give cation radical **27**, radical **28**, or cation **29**, respectively.

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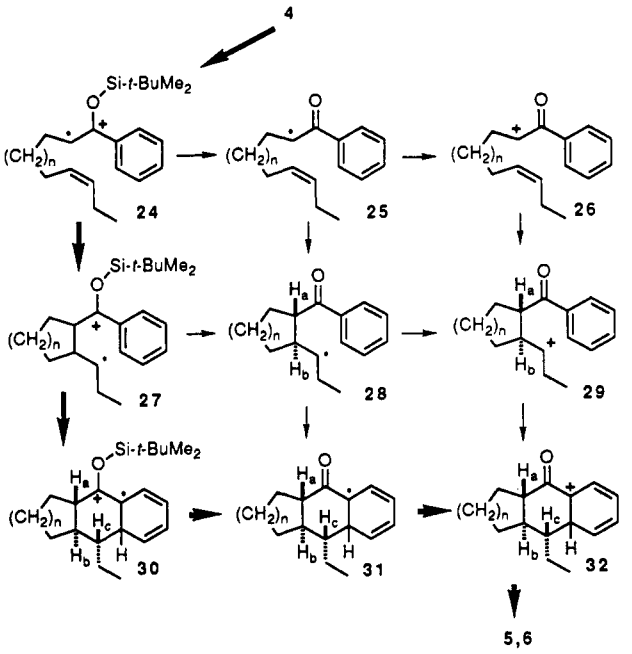
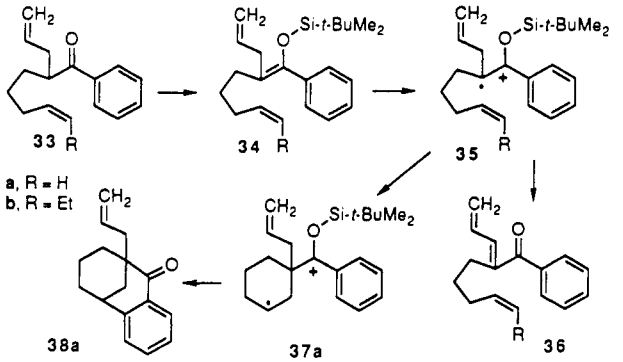


The cyclization of a free enol radical such as **25** in these oxidations is unlikely since Curran and Chang have shown that cyclization of the enol radical that would be generated from **13** by oxidation and loss of the silyl group gives a 3:1 mixture of 5-*exo* and 6-*endo* products,[28] while cyclization of **13** gives only 6-*endo* products. The cyclization of a free enol cation such as **26** in these oxidations is unlikely since enol cations analogous to **26** cyclize exclusively 6-*endo*, while we obtain exclusively 5-*exo* products from oxidation of **4**.[29] To unambiguously establish that **26** does not give **29**, we prepared the α-bromo ketone precursor to **26** by bromination of **1** with $CuBr_2$.[30] Treatment of the bromo ketone with $AgSbF_6$[29] provides no **5** or **6**.

By a process of elimination, the cyclization probably proceeds through cation radical **24** to give cyclic cation radical **27** since the cyclization does not proceed through radical **25** or cation **26**. The exclusive formation of 6-*endo* products from **13** and 5-*exo* products from **7a** is consistent with the expected behavior of a very electrophilic cation radical such as **24**. Cyclization of cation radicals has also been postulated in related electrochemical oxidative cyclizations.[11]

There are also three distinct possibilities for the second cyclization to form the tetralone ring. Cyclization of cation radical **27** could give cation radical **30**, which could lose a silyl group to give radical **31**. Oxidation of radical **31** could give cation **32**, which could lose a proton to give tetralones **5** and **6**. Alternatively, loss of a silyl group from **27** could give radical **28**, which could cyclize to give radical **31**. Finally, loss of a silyl group from **27** and oxidation could give cation **29**, which could cyclize to cation **32**. Cyclization of 4-phenyl-4-oxobutyl radicals followed by oxidation to give α-tetralones is well-known.[1a-c,2b] There is also ample precedent for the Friedel–Crafts cyclization of carbocations to aryl ketones to give α-tetralones.[1b,31]

We turned our attention to substrates containing a second double bond in an attempt to trap the monocyclic intermediate and provide information about the mechanism of tetralone formation. α-Allylation[32] of ketones **1** and **12** followed by silylation of the ketones **33a** and **33b** with Et_3N and TBDMSOTf affords silyl enol ethers **34a** and **34b**. To our disappointment, treatment of **34a** with CAN gives 60% of triene **36a** and 12% of tricyclic ketone **38a**. Oxidation of **34a** with $Cu(OTf)_2$ is even less successful, giving a complex mixture containing 7% of triene **36a**, 10% of tricyclic ketone **38a**, and 2% of ketone **33a**. Oxidation of **34b** with CAN gives 31% of triene **36b**, while oxidation with $Cu(OTf)_2$ gives no identifiable products.



The presence of the allyl group completely changes the course of the reaction. The major process is loss of an acidic allylic proton from the cation radical **35** leading to a pentadienyl radical, which is oxidized to a cation, which loses the silyl group to give triene **36**. Cyclization of **35a** to give **37a** is a minor process. It is noteworthy, that the second cyclization of **37a** occurs exclusively to the benzene ring and that no monocyclic products are obtained, while cyclization of **13** gives mainly monocyclic products. Cyclization of the monocyclic cation radical obtained from **13** to give **19** will be slow since the benzoyl group is predominantly equatorial. On the other hand, cyclization of **37a** should be fast since the benzoyl group is predominantly axial; the *A* value for the benzoyl group is 1.2 while the *A* value for the allyl group is 1.7.[33]

We turned our attention to silyl enol ether **43** in which the double bond was positioned so as not to interfere with the first cyclization. Alkylation[34] of the THP ether of 5-hexyn-1-ol with 5-bromo-1-pentene and hydrolysis[35] of the THP ether affords 81% of **39**. Reduction of the triple bond of **39** with iron filings[36] gives alcohol **40** containing a cis double bond. Tosylation of alcohol **40** followed by treatment of the resulting tosylate with NaCN affords nitrile **41**.[37] Addition of PhMgBr to **41** followed hydrolysis provides ketone **42**, which is treated with Et_3N and TBDMSOTf to give a 5:1 mixture of silyl enol ethers (*Z*)-**43** and (*E*)-**43**.

Oxidation of the 5:1 mixture of (*Z*)- and (*E*)-**43** with $Cu(OTf)_2$ affords 80% of a 4:1 mixture of tricyclic ketones **44** and **45**. To our surprise, the benzene ring participates in the second cyclization instead of the double bond. This observation suggests that the second cyclization is also taking place through cation radical intermediate **49**. As

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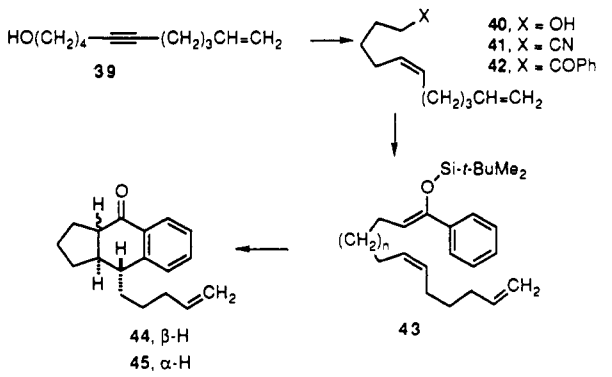
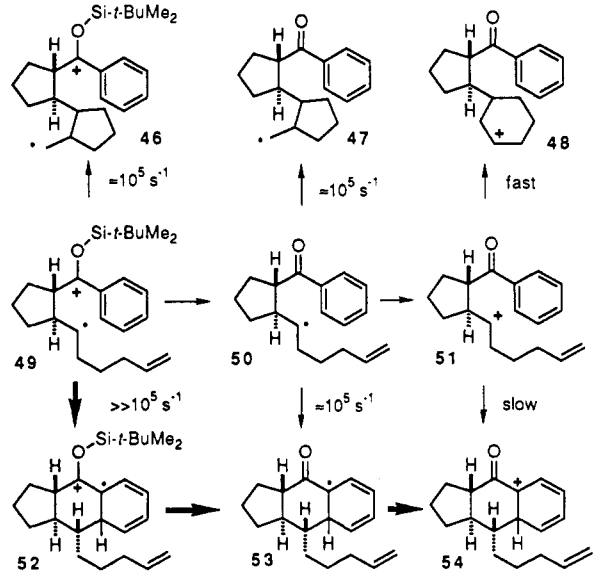
(29) Cambillau, C.; Charpentier-Morize, M. *J. Chem. Soc., Chem. Commun.* **1982**, 211.
(30) Glazier, E. R. *J. Org. Chem.* **1962**, *27*, 4397.
(31) (a) Khalaf, A. A.; Abdel-Wahab, A.-M.; El-Khawaga, A. M.; El-Zohry, M. F. *Bull. Soc. Chim. Fr.* **1984**, II-285. (b) Roberts, R. M.; Khalaf, A. A. *Fridel-Crafts Alkylation Chemistry*; Marcel Dekker: New York, 1984. (c) Olah, G. A. *Fridel-Crafts Chemistry*; Wiley: New York, 1973.
(32) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.
(33) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965.
(34) Swartz, M.; Waters, R. M. *Synthesis* **1972**, 567.
(35) Sargent, M. V.; Wangchareontrakul, S. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1171.
(36) Morris, S. G.; Magidman, P.; Herb, S. F. *J. Am. Oil. Chem. Soc.* **1972**, *49*, 505. Schrauzer, G. N.; Guth, T. D. *J. Am. Chem. Soc.* **1976**, *98*, 3508.
(37) Paquette, L. A.; Meisinger, R. H.; Wingard, R. E., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 2230.



discussed above, the initial cyclization gives cation radical **49**. Loss of the silyl group would give radical **50**. Oxidation of **50** would give cation **51**.

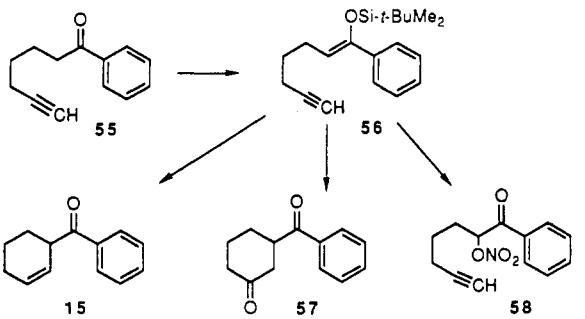
Cation **51** would be expected to cyclize preferentially to the double bond to give cyclohexyl cation **48**. Intramolecular Friedel–Crafts alkylations of unsaturated phenyl ketones must be carried out under drastic conditions due to the deactivating effect of carbonyl group.[31] Furthermore, olefinic double bonds are usually more reactive toward electrophilic agents than are aromatic rings.[38] Therefore **44** and **45** are probably not formed by the Friedel–Crafts cyclization of cation **51** to give **54**.



Radical **50** should cyclize to both the double bond and aromatic ring at similar rates. The rate constant for the cyclization of the radical to the double bond to give cyclopentylmethyl radical **50** is about 10^5 s^{-1}.[39] The rate constant for the cyclization to the aromatic ring of a radical analogous to **50** lacking the cyclopentane ring is 10^4 s^{-1}.[2b] Since Beckwith has shown that the presence of a cyclopentane ring in the tether increases the rate of the 5-hexenyl radical cyclization by 1 order of magnitude,[40] the rate of cyclization of **50** to give **53** should also be about 10^5 s^{-1}. This suggests that cyclization of the radical of **50** to the double bond and aromatic ring should occur at about the same rate. Since cyclization occurs exclusively to the aromatic ring, radical **50** is probably not an intermediate.

Since neither cation **51** nor radical **50** should give exclusively **44** and **45**, by a process of elimination, cation radical **49** probably cyclizes to give the tricyclic cation radical **52**, which then loses the silyl group, is oxidized, and is deprotonated to give **44** and **45**. Cyclization of cation radical **49** to give cyclopentanemethyl cation radical **46** should occur with a rate constant of about 10^5 s^{-1} since the positive charge should not effect the rate of this cyclization. On the other hand, cyclization of the cation radical to give **52** should be much faster than 10^5 s^{-1} since the nucleophilic radical should add to the electron-deficient benzene ring much more rapidly than radical **50** cyclizes to the parent phenyl ketone. Therefore cation radical **49** should cyclize exclusively to the aromatic ring as is observed.

Oxidative Cyclization of Silyl Enol Ethers of Alkynyl Aromatic Ketones. Since 5-hexynyl radicals cyclize readily, we decided to explore the oxidative cyclization of enol ethers containing triple bonds. Treatment of ketone **55**[41] with Et_3N and TBDMSOTf affords an 8:1 mixture of (*Z*)-**56** and (*E*)-**56**. Oxidation of this mixture with $Cu(OTf)_2$ gives a complex mixture containing ketone **15**. If oxygen is not carefully excluded, 3-benzoylcyclohexanone (**57**)[42] is also obtained. Oxidation of **56** with CAN affords 18% of **15**, 4% of recovered silyl enol ether **56**, and 38% of acyclic α-nitrooxy ketone **58**. Cyclization of the cation radical onto the triple bond is slower than cyclization onto the double bond since **58** is the major product, while the acyclic nitrooxy ketone is a very minor product in the oxidative cyclization of **13**. The formation of **15** is of considerable mechanistic significance since it could only arise by hydrogen abstraction by a cyclohexenyl radical. The formation of **15** is consistent with the cyclization of the cation radical analogous to **24**, or the radical analogous to **25**. Cyclization of the cation analogous to **26** would give a cyclohexenyl cation that could not be reduced to **15**.



We examined the oxidative cyclization of silyl enol ether **60** since much higher yields of products are obtained from **4a** than from **13**. Alkylation of the THP ether of 5-hexyn-1-ol with methyl iodide and hydrolysis of the THP ether gives 5-heptyn-1-ol. Tosylation of the alcohol, displacement of the tosylate with cyanide, and addition of PhMgBr to the nitrile provides ketone **59**. Reaction of the ketone with Et_3N and TBDMSOTf provides an 8:1 mixture of (*Z*)-**60** and (*E*)-**60**. Treatment of this mixture with 2.5 equiv of $Cu(OTf)_2$ results in incomplete consumption of starting material **60**, giving a complex mixture from which tricyclic ketone **64** was obtained in 30% yield. The formation of **64** requires four one-electron oxidations and the addition of a molecule of water. Oxidation of **60** with 6.5 equiv of $Cu(OTf)_2$, excess Cu_2O, and 3 equiv of H_2O in acetonitrile gives **64** in 70% yield. Under anhydrous conditions a complex mixture of products are obtained.

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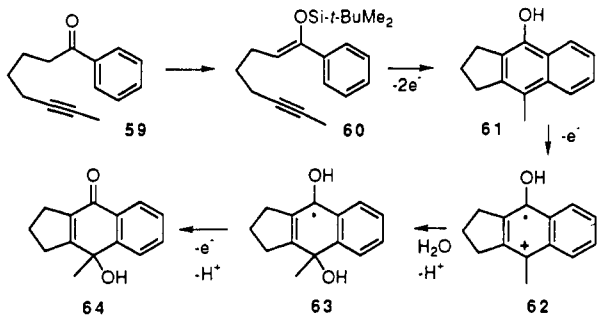
(39) (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon: Oxford, 1986. (b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925. (c) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron Lett.* **1985**, *26*, 373.
(40) Beckwith, A. L. J.; Phillipou, G.; Serelis, A. K. *Tetrahedron Lett.* **1981**, *22*, 2811.
(41) Gautier, J. A.; Miocque, M.; Mascrier-Demagny, L. *Bull. Soc. Chim. Fr.* **1967**, 1551.
(42) Seyden-Penne, J.; Seuron, N. *Tetrahedron* **1984**, *40*, 635.

Oxidation of **60** with 3 equiv of CAN provides 38% of **64**.



The spectral data of **64** are very similar to those of 4-hydroxy-4-methyl-2,5-cyclohexadien-1-one.[43] A plausible mechanism for the formation of **64** involves the oxidative cyclization of **60** to give naphthol **61**, which is strictly analogous to the formation of **5** from **4** except that the product benzocyclohexadienone tautomerizes to the phenol. Naphthol **61** can be oxidized to cation radical **62**, which can react with water and lose a proton to give radical **63**, which can be oxidized to give **64**. There is ample precedent for the oxidation of *p*-alkylphenols to 4-alkyl-4-hydroxy-2,5-cyclohexadien-1-ones by Tl(III) salts,[44a] CAN,[44b] $Pb(OAc)_4$,[44c] single oxygen,[43,44d] iodobenzene diacetate,[44e] Mn(III) acetylacetonate,[44f] and MnO_2.[44g]

Effect of Double Bond Stereochemistry on the Oxidative Cyclization of Silyl Enol Ethers. The oxidative cyclization of enol silyl ether (*Z*)-**4a** is highly stereospecific, giving 95% of **5a** and 5% of **6a**. If the cyclization proceeds through cation radical **24**, as we have proposed, different mixtures of products might be obtained from (*E*)-**4a**. If the cyclization proceeds through radical **25** or cation **26**, identical mixtures of products should be obtained from both (*E*)- and (*Z*)-**4a**. Unfortunately, pure (*E*)-**4a** could not be obtained by flash chromatography of the 5:1 mixture of (*Z*)-**4a** and (*E*)-**4a**, and alternative silylation procedures did not give more (*E*)-**4a**. Oxidative cyclization of a slightly enriched 3:2 mixture of (*Z*)- and (*E*)-**4a** with $Cu(OTf)_2$ affords a 4.5:1 mixture of **5a** and **6a** suggesting that (*E*)-**4a** gives mainly **6a**.

We therefore turned our attention to methyl enol ethers that could be prepared in pure *E* and *Z* forms. Treatment of ketone **1a** with $CH(OMe)_3$ adsorbed on Montmorillonite K10 clay in hexane gives the dimethyl ketal.[45] Treatment of the dimethyl ketal with TMSOTf and *i*-Pr_2NEt in CH_2Cl_2 affords a 1:1.8 mixture of methyl enol ethers (*Z*)-**65** and (*E*)-**65**.[46] Flash chromatography provides an 8:1 mixture of (*Z*)-**65** and (*E*)-**65**. Replacement of *i*-Pr_2NEt by Et_3N provided a 1:4.2 mixture of (*Z*)-**65** and (*E*)-**65**, which was enriched to a 1:10 mixture by flash chromatography. Oxidation of the 8:1 mixture of (*Z*)-**65** and (*E*)-**65** with $Cu(OTf)_2$ gives a 7:1 mixture of **5a** and **6a**. Similar treatment of the 1:10 mixture of (*Z*)-**65** and (*E*)-**65** affords a 1:7 mixture of **5a** and **6a**. Complex mixtures were obtained by oxidation of **65** with CAN.

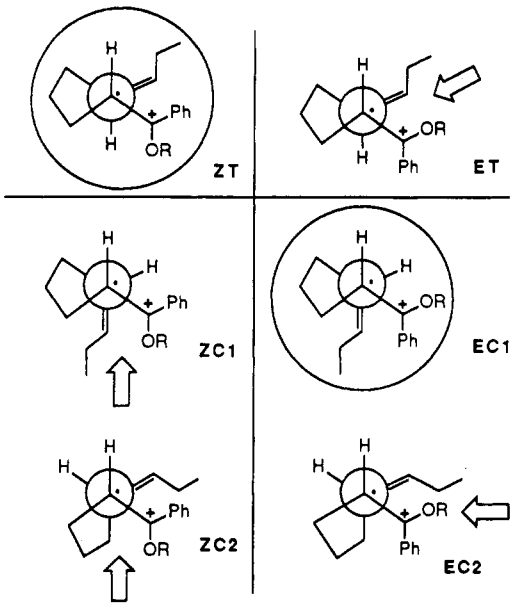
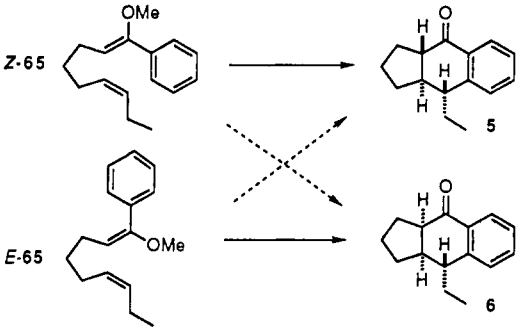


Figure 2. Possible transition states for the cyclization of **4** and **65**. The *Z*-isomer cyclizes to **5a** through **ZT**. The *E*-isomer cyclizes to **6a** through **EC1**.



These results establish that (*Z*)-**4a** and (*Z*)-**65** give predominantly the trans-fused ketone **5a**, while (*E*)-**4a** and (*E*)-**65** give mainly the cis-fused ketone **6a**. Therefore the cyclization must be proceeding through cation radical **24** that retains the geometry of the starting enol ether. Examination of Newman projections of the possible transition states for the cyclizations of the cation radicals provides a possible explanation for the observed stereoselectivity (see Figure 2). The cation radical derived from (*Z*)-**65** cyclizes through transition state **ZT** to give **5a** rather than through either **ZC1** or **ZC2** to give **6a**. The cation radical derived from (*E*)-**65** cyclizes through either **EC1** or **EC2** to give **6a** rather than through **ET** to give **5a**.

An examination of steric interactions suggests that this observation can be explained by postulating that the OR group is "large" so that **ZT** and **EC1** are preferred to minimize steric interactions. Why should the OR group be larger than a phenyl group? First, there must be an anion associated with the positive charge that is located largely on the oxygen atom. Second, the reduced metal salt may still be associated with the oxygen.

This model suggests that the alkene geometry is unimportant. Isomerization of the double bond of ketone **1a** with *p*-toluenesulfinic acid[47] provided a 5:1 *E*/*Z* mixture of **1a**. This mixture was converted to the (*Z*)-TBDMS enol ether and oxidized with $Cu(OTf)_2$ to give a 20:1 mixture

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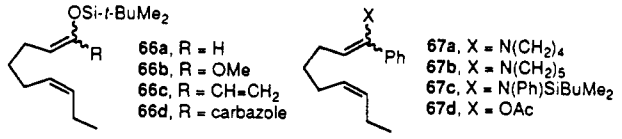
(44) (a) Yamada, Y.; Hosaka, K.; Sawahata, T.; Watanabe, Y.; Iguchi, K. *Tetrahedron Lett.* **1977**, 2675. Yamada, Y.; Hosaka, K.; Sanjoh, H.; Suzuki, M. *J. Chem. Soc., Chem. Commun.* **1974**, 66a. McKiilop, A.; Perry, D. H.; Edwards, M.; Antus, H.; Farkas, L.; Nógrádi, M.; Taylor, E. C. *J. Org. Chem.* **1976**, *41*, 282. D'Ambrosio, M.; Guerriero, A.; Pietra, F. *Helv. Chim. Acta* **1984**, *67*, 1484. (b) Hanson, R. M. Ph.D. Dissertation, Columbia University, New York, NY, 1983. (c) Hara, H.; Hosaka, M.; Hoshino, O.; Umezawa, B. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1169. (d) Sedee, A. G. J.; Beijerbergen van Henegouwen, G. M. J. *Tetrahedron Lett.* **1983**, *24*, 5779. (e) Lewis, N.; Wallbank, P. *Synthesis* **1987**, 1103. (f) Forrester, A.; Thomson, R. H.; Woo, S.-O. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2340. (g) Dietl, H.; Young, H. S. *J. Org. Chem.* **1972**, *37*, 1672.
(45) Taylor, E. C.; Chang, C.-S. *Synthesis* **1977**, 467.
(46) Gassman, P. G.; Burns, S. J. *J. Org. Chem.* **1988**, *53*, 5576.
(47) Gibson, T. W.; Strassburger, P. *J. Org. Chem.* **1976**, *41*, 791.

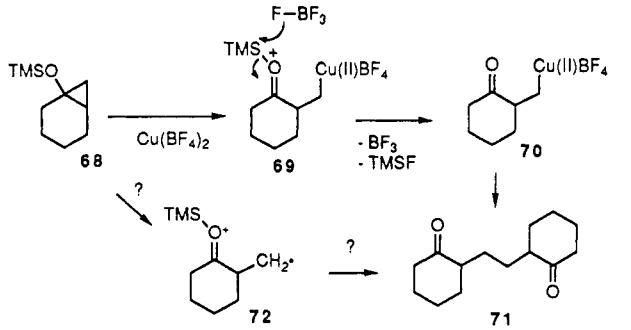
of **5a** and **6a**. Thus the alkene geometry has no effect on the stereoselectivity of the cyclization.

Attempted Oxidative Cyclization of Other Substrates. In an attempt to extend the scope of the reaction, we briefly examined the oxidative cyclization of other derivatives of phenyl ketone **1a** and the analogous aldehyde, ester, and α,β-unsaturated ketone. Complex mixtures are obtained by oxidation of **66a** with either $Cu(OTf)_2$ or CAN. Attempted oxidation of ketene silyl acetal **66b**[48] with either $Cu(OTf)_2$ or CAN in CH_3CN leads only to hydrolysis to give the methyl ester. Attempted oxidation of *tert*-butyldimethylsilyl enol ether **66c** with $Cu(OTf)_2$ or CAN also results in hydrolysis. Hydrolysis was also the major reaction on attempted oxidation of enamines **67a**,[49] **67b**[49] or **67c** with $Cu(OTf)_2$ or CAN. Enol acetate **67d**[50] does not react with CAN in CH_3CN. Although the oxidative dimerization of *N*-vinylcarbazoles via cation radical intermediates is well-known,[51] we were unable to obtain any cyclic products by oxidation of **66d**[52] with either $Fe(NO_3)_3$, $Cu(OTf)_2$, or CAN.

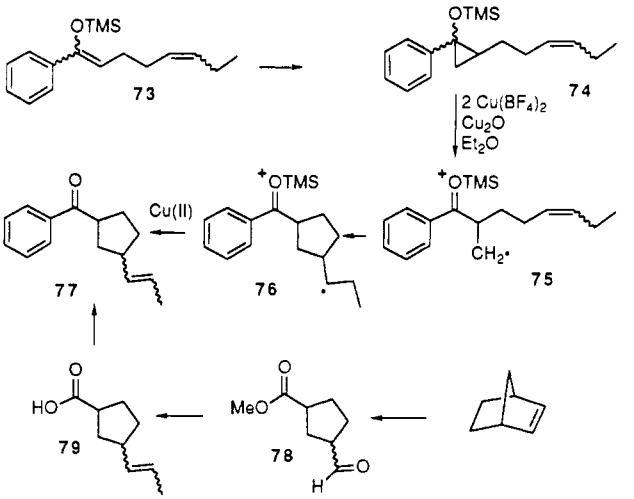


Formation of Radicals by Oxidative Cleavage of Siloxycyclopropanes. Murai and co-workers reported that treatment of siloxycyclopropane **68** with $AgBF_4$ or $Cu(BF_4)_2$ leads to the formation of 1,6-diketone **71**.[53] They proposed that the electrophilic attack of Ag^+ or Cu^{2+} at the least substituted carbon atom of **68** gives **69**, which loses Me_3SiF and BF_3 to give the β-metallo ketone **70**, which then dimerizes to afford 1,6-diketone **71**. The conditions for these reactions are remarkably similar to those of the oxidation of enol ethers with $Cu(OTf)_2$, which we have shown proceed through cation radicals. A possible first step in the oxidation of **68** might be formation of the cation radical **72**. We therefore set out to construct an unsaturated siloxycyclopropane that could give a 5-hexenyl cation radical that might cyclize to give the cyclopentanemethyl radical faster than it dimerizes to the 1,6-diketone.

In fact, the oxidation of cyclopropanols to give radicals is well-known. Oxidation of 1-methoxycyclopropanol with Fe(III) or Cu(II) gives $MeO_2CCH_2CH_2^{\bullet}$, which adds to electron-deficient alkenes.[54] Oxidation of cyclopropanols with Mn(III) 2-pyridinecarboxylate generates β-keto radicals, which add to electron rich silyl enol ethers.[55] Electrophilic ring opening of siloxycyclopropanes with $Hg(OAc)_2$, followed by reduction of the resulting organomercury compound with $NaBH_4$, is an efficient procedure for the generation of β-keto radicals under reductive conditions.[56]



Oxidation of *cis*-5-octen-1-ol with PCC in CH_2Cl_2 affords a mixture of *cis*- and *trans*-5-octen-1-al. The double bond isomerizes by a facile ene–retro ene process.[57] Addition of PhMgBr and Jones' oxidation of the resulting alcohol gives 1-phenyl-5-octen-1-one. Treatment of the ketone with TMSCl and DBU in CH_2Cl_2 gives enol ether **73**.[58] Cyclopropanation with $ZnEt_2$ and CH_2I_2 in Et_2O[59] affords a mixture of recovered **73**, siloxycyclopropane **74** (31%), and dicyclopropane.



Oxidation of **74** with 2 equiv of $Cu(BF_4)_2$ and excess Cu_2O in Et_2O gives a complex mixture whose ^1H NMR spectrum shows a broad doublet at δ 1.65 as expected for the allylic methyl group of **77**. Flash chromatography affords a fraction (21%) that appears to consist mainly of all four stereoisomers of **77** as determined by ^1H and ^{13}C NMR spectral and capillary GC analysis. An authentic sample of **77** was prepared to confirm the structure assignment.

Ozonolysis of norbornene by Schreiber's procedure[60] gives aldehyde ester **78**. Wittig olefination of **78** with ethyltriphenylphosphonium bromide and *n*-BuLi in THF and subsequent hydrolysis of the ester affords acid **79**, which is treated with 2 equiv of PhLi in ether to give a 6:8:7 mixture of the two stereoisomers of (*Z*)-**77** and the inseparable stereoisomers of (*E*)-**77**, respectively, as determined by capillary GC. Equilibration of this mixture with *p*-toluenesulfinic acid in dioxane at reflux[47] provides a 3:4:28 mixture of the two stereoisomers of (*Z*)-**77** and the inseparable stereoisomers of (*E*)-**77**, respectively. Analysis of the ^{13}C NMR spectra of this mixture indicates that (*E*)-**77**

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consists of a 2:3 mixture of stereoisomers. The ^1H and ^{13}C NMR and capillary GC data, including co-injection, of the authentic samples are identical with those of the products (*Z*)-**77** and (*E*)-**77** obtained from the oxidative cyclization of siloxycyclopropane **74**. Oxidation of **74** gives a 1:1:5 mixture of the two stereoisomers of (*Z*)-**77** and the inseparable stereoisomers of (*E*)-**77**. Analysis of the ^{13}C NMR spectra of the mixture indicated that (*E*)-**77** is a 1:1 mixture of stereoisomers.

A plausible mechanism for the formation of **77** is the oxidation of **74** by $Cu(BF_4)_2$ to generate cation radical **75**, which undergoes 5-*exo* cyclization to give cyclopentanealkyl radical **76**, which is oxidized by $Cu(BF_4)_2$ to variety of products including **77**. Although copper(II) carboxylates oxidize radicals to alkenes in high yield, $Cu(OTf)_2$ and $Cu(BF_4)_2$ give complex mixtures of products that are consistent with the formation of cationic intermediates.[5e] The cyclization of a 5-hexenylmetal intermediate analogous to **70** must also be considered. The cyclization of 5-hexenylmetals to give cyclopentylmethylmetals is known for lithium,[61] magnesium,[62] and aluminum.[63] The cyclization of 5-hexenylcopper(II) species related to those that would be formed in this reaction is not known. However, this is not necessarily significant since only alkylcopper(I) compounds have been extensively studied.

Conclusion. Oxidative cyclization of δ,ϵ- and ϵ,ζ-unsaturated enol silyl ethers **4a** and **4b** with cupric triflate and cuprous oxide or ceric ammonium nitrate and sodium bicarbonate in acetonitrile provides the tricyclic ketones **5a** and **5b** stereoselectively. These cyclizations proceed by oxidation of **4** to the cation radical **24** followed by cyclization of **24** to cation radical **27**. This cation radical undergoes a second cyclization to give cation radical **30**, which loses the silyl group, undergoes a second oxidation, and loses a proton to give **5**. The stereochemistry of the cycloadduct is controlled by the stereochemistry of the enol ether. The *Z*-enol methyl ether (*Z*)-**65** leads mainly to **5a** while the *E*-enol methyl ether (*E*)-**65** leads mainly to **6a**.

Oxidation of siloxycyclopropane **74** with $Cu(BF_4)_2$ generates cation radical **75**, which cyclizes to **76**, which is oxidized to give 21% of cyclopentane **77**. This suggests that cation radicals are intermediates in the oxidative dimerization of siloxycyclopropanes. However, the oxidative cyclization of siloxycyclopropanes containing a double bond is not synthetically useful because of the low yield and the difficulty in selective cyclopropanation of unsaturated silyl enol ethers.

Experimental Section

General. NMR spectra were recorded at 300 MHz in $CDCl_3$. Chemical shifts are reported in δ, and coupling constants in hertz. IR spectra are reported in cm^{-1}. All air-sensitive reactions were run under N_2 in flame-dried glassware with magnetic stirring. Reagents were added via oven-dried syringes through septa. CH_3CN was dried by distillation from calcium hydride. Cupric triflate was purchased from Fluka and used without purification. Cuprous oxide was purchased from Alfa.

Synthesis of 1-Phenyl-6(*Z*)-nonen-1-one (1a). A solution of 6-nonenal (1.67 g, 11.9 mmol) in 1 mL of ether was added dropwise at 0 °C to a solution of PhMgBr (3.0 M, 4.5 mL, 13.5 mmol) in ether. The solution was stirred overnight at 25 °C, poured into crushed ice, acidified with 5% H_2SO_4, and extracted with ether. The ether layer was dried ($MgSO_4$) and evaporated in vacuo to give 2.39 g of crude alcohol. Jones' reagent (1.4 M, 10 mL, 14.0 mmol) was added to a solution of crude alcohol (2.39 g) in 20 mL of acetone at 0 °C. The solution was warmed to 25 °C and stirred for 1.5 h. Saturated $NaHSO_3$ solution was added to the reaction mixture to destroy the remaining Cr(VI), and the solution was stirred until the color of Cr(VI) disappeared. The solution was extracted with ether, which was washed with saturated $NaHCO_3$ solution and saturated NaCl solution, dried ($MgSO_4$), and evaporated in vacuo to give 2.03 g of crude **1a**. Purification by flash chromatography on silica gel (9:1 hexane–EtOAc) gave 1.80 g (70%) of pure **1a**: ^1H NMR 7.96 (dd, 2, J = 8.0, 1.5), 7.54 (tt, 1, J = 7.0, 1.5), 7.46 (ddd, 2, J = 8.0, 7.0, 1.5), 5.37 (m, 2), 2.98 (t, 2, J = 7.4), 1.88–2.16 (m, 4), 1.76 (m, 2), 1.45 (m, 2), 0.96 (t, 3, J = 7.5); ^{13}C NMR 202.5, 137.0, 132.8, 132.0, 128.6, 128.5, 128.0, 38.4, 29.4, 26.9, 24.0, 20.5, 14.3; IR (neat) 3030, 2970, 2940, 2880, 169, 1603, 1585, 750, 690.

Synthesis of (1,1-Dimethylethyl)dimethyl[(1-phenyl-1-(*Z*),6(*Z*)-nonadienyl)oxy]silane [(*Z*)-4a] and (1,1-Dimethylethyl)dimethyl[(1-phenyl-1(*E*),6(*Z*)-nonadienyl)oxy]silane [(*E*)-4a]. Method A. A solution of TBDMSOTf (0.67 mL, 2.9 mmol) in 2 mL of CH_2Cl_2 was added at 25 °C to a solution of **1a** (216 mg, 0.99 mmol) and Et_3N (0.40 mL, 2.9 mmol) in 2 mL of CH_2Cl_2.[14] The solution was stirred at 25 °C for 2 h, diluted with ether, washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated in vacuo to give crude **4a**. Purification by flash chromatography on silica gel (hexane containing 0.5% pyridine) gave 292 mg (90%) of a 5:1 mixture of (*Z*)- and (*E*)-**4a**. Careful chromatography on silica gel (hexane) gave pure (*Z*)-**4a** and a more polar fraction containing a 3:2 mixture of (*Z*)- and (*E*)-**4a**.

Method B. To a solution of diisopropylamine (1.0 mL, 7.13 mmol) in 10 mL of THF at 0 °C was added a solution of *n*-BuLi (2.2 M, 3.3 mL, 7.26 mmol) in hexane, and the reaction mixture was stirred at 0 °C for 0.5 h. The LDA solution was cooled to −78 °C, and a solution of **1a** (1.50 g, 6.94 mmol) was added dropwise. The reaction mixture was stirred at −78 °C for 0.5 h and treated with TBDMSOTf (2.30 mL, 10.0 mmol).[15] The reaction mixture was stirred at −78 °C for 0.5 h and at 0 °C for 2 h and diluted with ether. The ether layer was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated in vacuo to give 2.5 g of crude **4a**. Flash chromatography on silica gel (hexane) deactivated with methanol gave 2.0 g (88%) of pure (*Z*)-**4a**.

The data for (*Z*)-**4a**: ^1H NMR 7.42 (dd, 2, J = 8.0, 1.2), 7.18–7.44 (m, 3), 5.38 (m, 2), 5.11 (t, 1, J = 7.2), 2.21 (m, 2), 1.95–2.16 (m, 4), 1.48 (tt, 2, J = 5.6, 5.6), 0.99 (s, 9), 0.98 (t, 3, J = 7.5), −0.04 (s, 6); ^{13}C NMR 149.4, 139.8, 131.9, 129.0, 127.9, 127.3, 125.9, 111.7, 29.8, 27.0, 25.9, 25.7, 20.5, 18.3, 14.4, −4.0; IR (neat) 3030, 2970, 2940, 2880, 1655, 1603, 1585, 750, 690. Anal. Calcd for $C_{21}H_{34}OSi$: C, 76.30; H, 10.37. Found: C, 76.17; H, 10.36.

Partial NMR data for (*E*)-**4a** were determined from the mixture: ^1H NMR 5.33 (m, 2), 5.08 (t, 1, J = 7.2), 2.21 (m, 2), 1.95–2.16 (m, 4), 1.45 (tt, 2, J = 5.6, 5.6), 0.94 (t, 3, J = 7.5), 0.92 (s, 9), 0.05 (s, 6); ^{13}C NMR 111.1.

Reaction of (*Z*)-4a with Cupric Triflate. A solution of (*Z*)-**4a** (113 mg, 0.34 mmol) in 5 mL of CH_3CN was slowly added over 5 h using a syringe pump to a solution of cupric triflate (250 mg, 0.69 mmol) and cuprous oxide (166 mg, 1.16 mmol) in 2 mL of CH_3CN at 0 °C. The resulting solution was stirred at 25 °C for 2–3 h, diluted with 20 mL of ether, acidified with 5% HCl solution, washed with saturated NaCl solution, dried ($MgSO_4$), and evaporated in vacuo to give 80 mg of crude product which was purified by flash chromatography on silica gel (9:1 hexane–EtOAc) to give 66 mg (90%) of an inseparable 20:1 mixture of (3aα,9β,9aβ)-9-ethyl-1,2,3,3a,9,9a-hexahydro-4*H*-benz[*f*]inden-4-one (**5a**) and (3aα,9α,9aα)-9-ethyl-1,2,3,3a,9,9a-hexahydro-4*H*-benz[*f*]inden-4-one (**6a**).

The data for **5a**: ^1H NMR 8.06 (dd, 1, J = 7.7, 1.4), 7.52 (ddd, 1, J = 7.9, 7.3, 1.4), 7.42 (br d, 1, J = 7.9), 7.31 (ddd, 1, J = 7.7, 7.3, 1.6), 2.96 (ddd, 1, J = 10.7, 3.8, 3.8, H_9), 2.51 (ddd, 1, J = 13.3, 9.8, 8.0, H_{3a}), 2.23 (dddd, 1, J = 13.3, 10.7, 7.3, 4.1, H_{9a}), 1.65–2.15 (m, 7), 1.49 (apparent br q, J = 7.4), 0.76 (t, 3, J = 7.4); ^{13}C NMR 200.2, 146.2, 134.9, 133.0, 127.3, 126.7, 126.2, 55.7, 46.6, 45.6, 30.7, 23.9, 22.9, 22.2, 8.1; IR (neat) 3080, 3040, 2990, 2885, 1695, 1605, 775. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.02; H, 8.34.

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Reaction of (*Z*)-4a with Ceric Ammonium Nitrate (CAN). A solution of (*Z*)-**4a** (39 mg, 0.12 mmol) in 2.5 mL of CH_3CN was slowly added over 3 h using a syringe pump to a solution of CAN (130 mg, 0.24 mmol) and sodium bicarbonate (40 mg, 0.48 mmol) in 1 mL of CH_3CN at 25 °C. The solution was stirred at 25 °C for 2–3 h, diluted with 10 mL of ether, acidified with 5% HCl solution, washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated in vacuo to give 32 mg of crude product which was purified by flash chromatography on silica gel (9:1 hexane–EtOAc) to give 18.5 mg (73%) of a 20:1 mixture of **5a** and **6a**.

Equilibration of 5a and 6a. A solution of the 20:1 mixture of **5a** and **6a** (22.3 mg) in 1 mL of 1 N KOH solution in methanol was stirred for 3 h. The reaction mixture was diluted with 10 mL of water and extracted with ether (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated in vacuo to give an inseparable 1:7.7 mixture of **5a** and **6a**. The data for **6a** were determined from the mixture: ^{1}H NMR 7.92 (dd, 1, J = 8, 1), 7.48 (ddd, 1, J = 8, 8, 1), 7.30 (ddd, 1, J = 8, 8, 1), 7.24 (dd, J = 8, 1), 3.01 (ddd, 1, J = 8, 8, 4, H_9), 2.78 (ddd, 1, J = 7, 7, 1.5, H_{3a}), 2.53 (dddd, 1, J = 11, 8, 7, 2, H_{9a}), 2.05 (m, 2), 1.65–1.90 (m, 2), 1.35–1.65 (m, 2), 1.22–1.35 (m, 2), 0.93 (t, 3, J = 7.6); ^{13}C NMR 202.0, 146.5, 133.0, 131.5, 129.9, 127.3, 126.7, 47.2, 43.4, 43.0, 32.2, 31.4, 31.2, 24.0, 12.3; IR (neat) 3080, 3040, 2970, 2880, 1685, 1608, 760.

Synthesis of (1,1-Dimethylethyl)dimethyl[(1-phenyl-1-(*Z*),7(*Z*)-decadienyl)oxy]silane [(*Z*)-4b]. Ketone **1b** (228 mg, 0.99 mmol) was converted to 306.8 mg (90%) of (*Z*)-**4b** as described in method B: ^{1}H NMR 7.44 (dd, 2, J = 8.0, 1.4), 7.16–7.33 (m, 3), 5.35 (m, 2), 5.10 (t, 1, J = 7.1), 2.15–2.25 (m, 2), 1.96–2.11 (m, 4), 1.36–1.46 (m, 4), 0.97 (s, 9), 0.93 (t, 3, J = 7.5), –0.05 (s, 6); ^{13}C NMR 149.2, 139.8, 131.6, 129.2, 127.8, 127.3, 125.8, 111.9, 29.6, 29.3, 27.0, 26.0, 25.9, 20.5, 18.3, 14.4, –4.0; IR (neat) 3003, 2960, 2930, 2860, 1603, 1560, 775, 690. Anal. Calcd for $C_{22}H_{36}OSi$: C, 76.67; H, 10.53. Found: C, 76.57; H, 10.53.

Oxidation of (*Z*)-4b with Cupric Triflate. A solution of (*Z*)-**4b** (220 mg, 0.64 mmol) in 5 mL of CH_3CN was slowly added over 5 h using a syring pump to a solution of cupric triflate (500 mg, 1.38 mmol) and cuprous oxide (332 mg, 2.32 mmol) in 2 mL of CH_3CN at 0 °C. The resulting solution was stirred at 25 °C for 2–3 h and worked up as described above to give 207 mg of crude product which was purified by flash chromatography on silica gel (9:1 hexane–EtOAc) to give 126 mg (87%) of a >20:1 mixture of (4aα,9aβ,10α)-10-ethyl-1,3,4,4a,9a,10-hexahydro-9-(2*H*)-anthracenone (**5b**) and (4aα,9aα,10α)-10-ethyl-1,3,4,4a,9a,10-hexahydro-9(2*H*)-anthracenone (**6b**).

The data for **5b**: ^{1}H NMR 8.01 (dd, 1, J = 7.8, 1.4), 7.52 (ddd, 1, J = 8.0, 7.3, 1.4), 7.41 (br d, 1, J = 8.0), 7.29 (ddd, 1, J = 7.8, 7.3, 1.1), 2.88 (ddd, 1, J = 10.4, 3.6, 3.6, H_{10}), 2.37 (m, 1), 2.08–2.27 (m, 3), 1.93–1.98 (m, 1), 1.65–1.93 (m, 3), 1.08–1.40 (m, 4), 0.70 (t, 3, J = 7.4); ^{13}C NMR 200.1, 145.1, 133.3, 133.2, 127.1, 126.6, 126.1, 50.9, 43.8, 40.6, 31.2, 26.1, 25.6, 25.3, 20.5, 7.60; IR (neat) 3060, 3040, 2940, 2860, 1670–1700, 1605, 765. Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.19; H, 8.78.

Reaction of (*Z*)-4b with CAN. A solution of (*Z*)-**4b** (80 mg, 0.23 mmol) in 5 mL of CH_3CN was slowly added over 5 h using a syringe pump to a solution of CAN (347 mg, 0.63 mmol) and sodium bicarbonate (100 mg, 1.19 mmol) in 3 mL of CH_3CN at 25 °c. The resulting solution was stirred at 25 °C for 2–3 h and worked up as described above to give 57.3 mg of crude product which was purified by flash chromatography on silica gel (9:1 hexane–EtOAc) to give 22.3 mg (42%) of a 4.3:1 mixture of **5b** and **6b** and 1.6 mg (3%) of a compound tentatively identified as the acyclic α-nitrooxy ketone[64] based on the absorbtion at δ 6.02 (dd, 1, J = 8.5, 4.1).

Equilibration of 5b and 6b. A solution of the above >20:1 mixture of **5b** and **6b** (35.9 mg) in 1 mL of 1 N KOH solution in methanol was stirred for 3 h. The reaction mixture was diluted with 10 mL of water and extracted with ether (3 × 10 mL). The combined ether layers were dried ($MgSO_4$) and evaporated in vacuo to give a 1:2.43 mixture of **5b** and **6b**. Flash chromatography on silica gel (9:1 hexane–EtOAc) gave 16.5 mg of pure **6b**, followed by 15.3 mg of mixed fractions followed by 1.0 mg of pure **5b**.

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The data for **6b**: ^{1}H NMR 8.04 (dd, 1, J = 7.8, 1.0), 7.46 (ddd, 1, J = 7.6, 7.5, 1.5), 7.29 (ddd, 1, J = 7.8, 7.5, 1.0), 7.19 (dd, 1, J = 7.6, 1.5), 2.93 (br s, 1, $W_{1/2}$ = 10), 2.62 (br d, J = 12), 2.53 (br dd, 1, J = 7, 7), 2.24 (m, 1), 1.42–1.86 (m, 5), 1.10–1.42 (m, 4), 1.05 (t, 3, J = 7.4); ^{13}C NMR 199.6, 146.8, 133.2, 131.1, 129.9, 127.1, 126.4, 47.0, 43.0, 40.5, 30.1, 29.1, 26.3, 26.0, 22.8, 12.8; IR 3060, 3040, 2940, 2860, 1670–1700, 1605, 765. Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.95; H, 8.85.

Synthesis of (1,1-Dimethylethyl)dimethyl[(1-phenyl-3,7-dimethyl-1(*Z*),6-octadienyl)oxy]silane [(*Z*)-7]. 3,7-Dimethyl-1-phenyl-6-octen-1-one (230 mg, 1.00 mmol) was converted to 305 mg (90%) of an 8:1 mixture of (*Z*)- and (*E*)-**7** as described in method A. Careful flash chromatography on silica gel (hexane) gave pure (*Z*)-**7**: ^{1}H NMR 7.39–7.45 (m, 2), 7.20–7.30 (m, 3), 5.14 (tqq, 1, J = 7.2, 1.4, 1.2), 4.86 (d, 1, J = 9.7), 4.80 (d, 1, J = 9.7, (*E*)-**7**), 2.62–2.77 (m, 1), 1.95–2.05 (m, 2), 1.68 (d, 3, J = 1.4), 1.60 (br s, 3), 1.28–1.40 (m, 2), 1.01 (d, 3, J = 6.8), 0.98 (s, 9), –0.05 (s, 6); ^{13}C NMR 148.5, 140.1, 131.0, 127.8, 127.3, 126.2, 125.0, 118.4, 37.9, 30.0, 26.1, 25.9, 25.8, 20.8, 18.3, 17.6, –2.9; IR (neat) 3060, 3030, 2960, 2920, 2850, 1653, 1580, 770, 690 cm^{-1}. Anal. Calcd for $C_{22}H_{36}OSi$: C, 76.23; H, 10.47. Found: C, 76.03; H, 10.46.

Reaction of (*Z*)-7 with Cupric Triflate. A solution of (*Z*)-**7** (141 mg, 0.41 mmol) in 5 mL of CH_3CN was slowly added over 5 h using a syringe pump to a solution of cupric triflate (300 mg, 0.82 mmol) and cuprous oxide (200 mg, 1.4 mmol) in 2 mL of CH_3CN at 0 °C. The resulting solution was stirred at 25 °C for 2–3 h and worked up as described above to give 126 mg of crude product which was purified by flash chromatography on silica gel (9:1 hexane–EtOAc) to give 49.5 mg of (3α,3aα,9$\alpha\beta$)-1,2,3,3a,9,9a-hexahydro-3,9,9-trimethyl-4*H*-benz[*f*]inden-4-one (**8**), followed by 27.2 mg of mixed fractions and 6.4 mg of (3α,3aα,9α)-1,2,3,3a,9,9a-hexahydro-3,9,9-trimethyl-4*H*-benz[*f*]-inden-4-one (**9**) (83.1 mg (90%) of a 3.2:1 mixture of **8** and **9**).

The data for **8**: ^{1}H NMR 8.00 (ddd, 1, J = 8.8, 1.6, 1.0), 7.51 (ddd, 1, J = 7.7, 7.0, 1.6), 7.46 (ddd, 1, J = 7.0, 1.5, 1.0), 7.28 (ddd, 1, J = 8.8, 7.7, 1.5), 2.36 (m, 1, H_3), 2.26 (dd, 1, J = 13.6, 8.7, H_{3a}), 2.15 (ddd, 1, J = 13.6, 10.9, 7.1, H_{9a}), 1.95 (dddd, 1, J = 10.8, 8.0, 7.1, 6.5), 1.80 (dddd, 1, J = 10.3, 7.1, 5.4, 2.7), 1.5–1.7 (m, 2), 1.39 (s, 3), 1.26 (s, 3), 1.24 (d, 3, J = 6.5); ^{13}C NMR 200.1, 153.7, 133.2, 132.5, 126.9, 126.3, 126.2, 55.8, 53.2, 37.7, 33.3, 31.7, 28.6, 24.7, 23.2, 21.5; IR (neat) 3075, 3040, 2970, 2880, 1700, 1608, 760. Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.18; H, 8.96.

The data for **9**: ^{1}H NMR 7.86 (dd, 1, J = 7.6, 1.4), 7.51 (ddd, 1, J = 7.9, 7.3, 1.4), 7.36 (br d, 1, J = 7.9), 7.30 (ddd, 1, J = 7.6, 7.3, 1.2), 2.66 (dd, 1, J = 8.2, 5.5, H_{3a}), 2.42 (ddd, 1, J = 11.5, 8.2, 7.0, H_{9a}), 2.18 (m, 1, H_3), 1.70–1.90 (m, 2), 1.43 (s, 3), 1.25 (s, 3), 1.21 (d, 3, J = 6.8), 1.0–1.30 (m, 2); ^{13}C NMR 202.0, 150.2, 133.4, 132.0, 127.4, 126.3, 125.3, 55.7, 50.4, 40.6, 36.0, 34.6, 34.1, 29.4, 26.0, 21.4; IR (neat) 3075, 3040, 2970, 2880, 1700, 1608, 760. Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.12; H, 8.96.

Reaction of (*Z*)-7 with CAN. A solution of (*Z*)-**7** (210 mg, 0.606 mmol) in 5 mL of CH_3CN was slowly added over 5 h using syringe pump to a solution of CAN (997 mg, 1.819 mmol) and sodium bicarbonate (210 mg, 2.450 mmol) in 9 mL of CH_3CN at 25 °C. The solution was stirred at 25 °C for 2–3 h and worked up as described above to give 152 mg of crude product. Purification by flash chromatography on silica gel (9:1 hexane–EtOAc) gave 101 mg (73%) of a 3:1 mixture of **8** and **9**.

Synthesis of (1,1-Dimethylethyl)dimethyl[(1-phenyl-1-(*Z*),6-heptadienyl)oxy]silane [(*Z*)-13]. Ketone **12**[23] (250 mg, 1.36 mmol) was converted to 250 mg of pure (*Z*)-**13** and 70 mg of a 2:1 mixture of (*Z*)- and (*E*)-**13** (combined yield 85%) as described in method A.

The data for (*Z*)-**13**: ^{1}H NMR 7.48 (dd, 1, J = 8.3, 1.5), 7.49 (t, 1, J = 8.3), 5.89 (ddt, 1, J = 17.1, 9.1, 7.2), 5.16 (t, 1, J = 7.2), 5.08 (ddt, 1, J = 17.1, 2.1, 7.2), 5.02 (ddt, 1, J = 9.1, 2.1, 1.0), 2.27 (dt (apparent q), 2, J = 7.2, 7.5), 2.15 (dddt, 2, J = 7.2, 1.5, 1.0, 7.5), 1.57 (tt (apparent quintet), 2, J = 7.5, 7.5), 1.04 (s, 9), –0.05 (s, 6); ^{13}C NMR 149.8, 140.2, 139.2, 128.2, 127.7, 126.2, 114.8, 111.9, 34.0, 29.3, 26.2, 26.1, 18.7, –4.0; IR (neat) 3080, 3060, 2950, 2930, 2860, 1675, 1645, 1603, 1580, 745, 685. Anal. Calcd for $C_{19}H_{30}OSi$: C, 75.43; H, 10.00. Found: C, 75.25; H, 9.97.

Partial data for (*E*)-**13** were obtained from mixture: ^{1}H NMR 5.82 (m, 2), 5.07 (t, 1, J = 7.2), 5.01 (ddt, 1, J = 17.1, 2.1, 7.2), 4.95 (ddt, 1, J = 9.1, 2.1, 1.0), 2.27 (dt (apparent q), 2, J = 7.2, 7.5), 2.08 (dddt, 2, J = 7.2, 1.5, 1.0, 7.5), 1.52 (tt (apparent quintet),

1, J = 7.5, 7.5), 0.97 (s, 9), 0.03 (s, 6).

Reaction of (*Z*)-13 with Cupric Triflate. A solution of (*Z*)-**13** (162 mg, 0.536 mmol) in 5 mL of CH_3CN was slowly added over 8 h using a syringe pump to a solution of cupric triflate (390 mg, 1.078 mmol) and cuprous oxide (260 g, 1.82 mmol) in 4 mL of CH_3CN at 0 °C. The resulting solution was stirred at 25 °C for an additional 0.5 h and worked up as described above to give 300 mg of crude product. Purification by flash chromatography on silica gel (9:1 hexane–EtOAc) gave 11.7 mg of a 2:1 mixture of (3-cyclohexen-1-yl)phenylmethanone (**16**) and **12** and 17.4 mg of a 7:9:4:2 mixture of **16**, 6,7,8,9-tetrahydro-5,9-methanobenzocyclooctene-10(5*H*)-one (**19**), **12**, and 1-cyclohexen-1-ylphenylmethanone (**14**).

The data for **16**: ^{1}H NMR 7.97 (dddd, 2, J = 8.1, 1.4, 1.3, 1.0), 7.57 (dddd, 1, J = 7.3, 7.3, 1.4, 1.4), 7.47 (dddd, 2, J = 8.1, 7.3, 2.0, 1.3), 5.76 (br s, 2), 3.54 (dddd, 1, J = 11.5, 10.3, 5.2, 2.7), 2.28–2.45 (m, 1), 1.90–2.05 (m, 1), 1.65–1.90 (m, 1); ^{13}C NMR 203.4, 136.2, 132.9, 128.6, 128.3, 126.6, 125.7, 41.5, 27.9, 25.7, 24.9; IR (neat) 3030, 2940, 2850, 1690, 1603, 1587, 695. The data are identical to those previously described.[24]

The data for **19**: ^{1}H NMR 8.02–8.06 (m, 1), 7.47–7.54 (m, 1), 7.22–7.38 (m, 2), 3.17 (m, 1), 2.74 (m, 1), 2.37 (br d, 1, J = 12.7), 2.00 (dt, 1, J = 12.7, 4.8), 1.82–1.95 (m, 1), 1.67–1.82 (m, 1), 1.38–1.82 (m, 1), 1.10–1.38 (m, 2), 0.77–0.93 (m, 1). These data are identical to those previously described.[25]

The structure of **14** was assigned by comparison with an authentic sample prepared by the $AgSbF_6$-induced reaction of benzoyl chloride with cyclohexene.[24,26]

Reaction of (*Z*)-13 with CAN. A solution of (*Z*)-**13** (500 mg, 1.65 mmol) in 20 mL of CH_3CN was slowly added over 8 h using a syringe pump to a solution of CAN (2.00 g, 3.65 mmol) and sodium bicarbonate (500 mg, 5.95 mmol) in 15 mL of CH_3CN at 25 °C. The solution was stirred at 25 °C for additional 3 h and worked up as described above to give 380 mg of crude product. Purification by flash chromatography on silica gel (9:1 hexane–EtOAc) gave 74.5 mg of a 26.4:1:1 mixture of **16**, **12**, and 2-cyclohexen-1-ylphenylmethanone (**15**); 16.1 mg of a 20:2:1 mixture of **16**, **12**, and **15**; 5.7 mg of a 5:1 mixture of **16** and **15**; 9.8 mg of a 3:1 mixture of *trans*-[3-(nitrooxy)cyclohexyl]phenylmethanone (**18**) and **19**; 43.2 mg of a 10:1:trace mixture of **18**, **19**, and the acyclic α-nitrooxy ketone; 43.6 mg of **18**; 67.6 mg of a 1:1 mixture of **18** and *cis*-[3-(nitrooxy)cyclohexyl]phenylmethanone (**17**); and 32.0 mg of **17**.

The data for **15**: ^{1}H NMR (7.96 (dddd, 2, J = 7.1, 1.5, 1.5, 1.3), 7.56 (dddd, 1, J = 7.2, 7.2, 1.8, 1.3), 7.47 (dddd, 2, J = 7.2, 7.1, 1.5, 1.3), 5.93 (m, 1), 5.73 (ddd, 1, J = 10.2, 4.2, 1.1), 4.09 (m, 1), 1.50–2.20 (m, 6); ^{13}C NMR 201.8, 136.2, 133.2, 130.5, 129.0, 128.9, 125.1, 44.3, 26.2, 25.2, 21.3; IR (neat) 3060, 3030, 2930, 2860, 1680, 1600, 1580. The spectral data were identical with those of an authentic sample prepared by the $AgSbF_6$-induced reaction of benzoyl chloride with cyclohexene.[26]

The data for **18**: ^{1}H NMR 7.95 (dddd, 2, J = 8.0, 1.9, 1.3, 0.6), 7.58 (apparent tt, 1, J = 7.3, 1.3), 7.48 (dddd, 2, J = 8.0, 7.3, 0.8, 0.6), 5.45 (dddd, 1, J = 3.1, 3.1, 3.1, 3.1), 3.69 (dddd, 1, J = 11.0, 11.0, 3.9, 3.9), 1.80–2.40 (m, 4), 1.30–1.90 (m, 4); ^{13}C NMR 202.2, 135.5, 133.5, 128.8, 128.3, 79.4, 39.9, 30.7, 28.8, 28.2, 20.2; IR (neat) 3070, 2970, 2880, 1690, 1630, 1603, 1587, 1278, 695. Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07. Found: C, 62.37; H, 5.97.

The data for **17**: ^{1}H NMR 7.94 (dddd, 2, J = 8.0, 1.9, 1.3, 0.6), 7.59 (apparent tt, 1, J = 7.3, 1.3), 7.49 (dddd, 2, J = 8.0, 7.3, 0.8, 0.6), 5.06 (dddd, 1, J = 11.2, 11.2, 4.2, 4.2), 3.45 (dddd, 1, J = 12.0, 12.0, 3.4, 3.4), 2.28 (br d, 1, J = 12.4), 2.19 (br d, 1, J = 11.9), 2.04 (dddd (apparent dq), 1, J = 12.9, 3.4), 1.96 (br d, 1, J = 13.3), 1.72 (ddd (apparent q), 1, J = 12.4, 12.0, 11.2), 1.59 (ddddd (apparent qt), 1, J = 12.7, 3.2), 1.47 (dddd (apparent td), 1, J = 11.7, 3.2), 1.38 (dddd (apparent td), 1, J = 12.7, 3.5); ^{13}C NMR 200.8, 135.6, 133.3, 128.8, 128.2, 82.0, 43.6, 32.1, 29.5, 28.6, 23.6; IR (neat) 3070, 2970, 2880, 1690, 1630, 1603, 1587, 1278, 695. Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07. Found: C, 62.80; H, 6.20.

Synthesis of (1,1-Dimethylethyl)dimethyl[(2,2,5,9-tetramethyl-3(*Z*),8-decadienyl)oxy]silane (21a). Ketone **20** (3.66 g, 17.4 mmol) was converted to 4.63 g (82%) of an inseparable 10:1 mixture of (*Z*)- and (*E*)-**21a** as described in method A: ^{1}H NMR 5.10 (tqq, 1, J = 7.2, 1.4, 1.2), 4.26 (d, 1, J = 9.9), 2.36–2.52 (m, 1), 1.88–1.99 (br dt, 2, J = 7.5, 7.2), 1.67 (br s, 3), 1.59 (br s, 3), 1.11–1.34 (m, 2), 1.14 (s, 9, (*E*)-**21a**), 1.05 (s, 9), 0.96 (s, 9), 0.89 (d, 3, J = 6.6), 0.18 (s, 3), 0.16 (s, 3), 0.15 (s, 3, (*E*)-**21a**), 0.13 (s, 3, (*E*)-**21a**); ^{13}C NMR 156.4, 130.9, 125.2, 110.2, 38.3, 36.4, 29.1, 29.0, 26.5, 25.9, 25.7, 21.3, 19.3, 17.6, -2.9, -3.3; IR (neat) 2975, 2940, 2885, 1668.

Reaction of 21a with CAN. A solution of **21a** (423 mg, 1.30 mmol) in 20 mL of CH_3CN was slowly added over 3.5 h using a syringe pump to a solution of CAN (2.00 g, 3.65 mmol) and sodium bicarbonate (12.5 g, 14.9 mmol) in 15 mL of CH_3CN at 25 °C. The solution was stirred at 25 °C for additional 3.5 h and worked up as described above to give 350 mg of crude product. Purification by flash chromatography on silica gel (9:1 hexane–ether) gave 117.3 mg (40%) of an inseparable 1:1 mixture of **20** and 2,2-dimethyl-1-[(1α,2β,5β)-2-methyl-5-(1-methylethenyl)cyclopentyl]-1-propanone (**22**) and 5 mg (1.8%) of *trans*-2,2-dimethyl-1-[2-methyl-5-(1-methylethylidene)cyclopentyl]-1-propanone (**23**).

Pure **22** was obtained by preparative GC (10-ft. × $^3/_8$-in. 20% carbowax 20 M on Chromosorb PNAW, 150 °C): ^{1}H NMR 4.71 (dd, 1, J = 1.5, 0.6), 4.66 (dq, 1, J = 4.7, 1.4), 2.80–2.91 (m, 2), 2.18 (dddq, 1, J = 7.3, 7.3, 7.3, 6.8), 1.77–1.97 (m, 2), 1.71 (dd, 3, J = 1.4, 0.7), 1.57–1.70 (m, 1), 1.27–1.41 (m, 1), 1.08 (s, 9), 1.00 (d, 3, J = 6.8); ^{1}H NMR (C_6D_6) 4.81 (dd, 1, J = 1.5, 0.6), 4.70 (dq, 1, J = 5.0, 1.4), 3.09 (ddd, 1, J = 8.6, 8.2, 8.2), 2.77 (dd, 1, J = 8.6, 7.3), 2.31 (dddq, 1, J = 7.3, 7.3, 7.3, 6.8), 1.76–1.92 (m, 2), 1.60 (dd, 3, J = 1.4, 0.7), 1.48–1.59 (m, 1), 1.14–1.29 (m, 1), 1.07 (s, 9), 0.90 (d, 3, J = 6.8); ^{13}C NMR (carbonyl peak not seen), 146.7, 111.3, 57.2, 54.4, 44.0, 41.4, 34.5, 30.5, 26.0, 20.1, 19.4. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.54; H, 11.88.

The data for **23**: ^{1}H NMR 3.59 (br s, 1), 2.24–2.48 (m, 2), 2.10–2.20 (m, 1), 1.97 (m, 1), 1.66 (br s, 3), 1.54 (br s, 3), 1.22 (s, 9), 1.00 (d, 3, J = 6.8), 1.00–1.50 (m, 1).

Synthesis of (1,1,2-Trimethylpropyl)dimethyl[(2,2,5,9-tetramethyl-3(*Z*),8-decadienyl)oxy]silane (21b). Ketone **20** (2.0 g, 9.51 mmol) was converted to 2.94 g (90%) of an inseparable 4:1 mixture of (*Z*)- and (*E*)-**21b** as described in method A using dimethylthexylsilyl triflate instead of *tert*-butyldimethylsilyl triflate:[27] ^{1}H NMR 5.11 (tqq, 1, J = 7.2, 1.4, 1.2), 4.26 (d, 1, J = 9.9), 4.24 (d, 1, J = 9.9 (*E*)-**21b**), 2.37–2.53 (m, 1), 1.88–1.99 (br dt, 2, J = 7.5, 7.2), 1.76 (septet, 1, J = 7.0), 1.67 (br d, 3, J = 1.1), 1.58 (br s), 1.11–1.34 (m, 2), 1.13 (s, 9, (*E*)-**21b**), 1.05 (s, 9), 0.78–0.95 (4 CH_3), 0.20 (s, 3), 0.19 (s, 3, (*E*)-**21b**), 0.18 (s, 3), 0.17 (s, 3, (*E*)h**21b**); ^{13}C NMR [(*Z*)-**21b**] 156.3, 130.9, 125.2, 110.4, 38.3, 36.3, 33.7, 29.1, 26.0, 25.9, 25.7, 21.3, 20.7, 20.5, 20.1, 18.6, 18.4, 18.3, -1.3, -1.5.

Reaction of 21b with CAN. To a solution of CAN (920 mg, 1.68 mmol) and $NaHCO_3$ (6.0 g, 71.4 mmol) in 9 mL of CH_3CN was added a solution of **21b** (250 mg, 0.734 mmol) in 3 mL of CH_3CN. The reaction mixture was stirred at rt overnight, diluted with 70 mL of water, extracted with petroleum ether (3 × 25 mL), washed with sodium bicarbonate solution, dired ($MgSO_4$) and evaporated in vacuo at -5 to -10 °C to give 198 mg of crude **22**, which was purified by flash chromatography on silica gel (9:1 pentane–ether) to give 63.4 mg of a 1:3 mixture of **20** (14%) and **22** (42%).

Synthesis of (1,1-Dimethylethyl)dimethyl[(1-phenyl-2-(2-propenyl)-1,6-heptadienyl)oxy]silane (34a). To a solution of **33a** (400 mg, 1.75 mmol) and Et_3N (0.51 mL, 3.66 mmol) in 8 mL of CH_2Cl_2 was added TBDMSOTf (0.42 mL, 1.83 mmol), and the solution was stirred overnight. An additional 0.2 mL of TBDMSOTf was added. The resulting solution was stirred for 2 h and heated at reflux for 1 h. Normal workup and purification by flash chromatography on silica gel (hexane) gave 200 mg (33%) of an inseparable 5:4 mixture of (*Z*)- and (*E*)-**34a** and 200 mg (50%) of recovered **33a**: ^{1}H NMR ($CDCl_3$) 7.20–7.36 (m, 5), 5.60–5.96 (m, 2), 4.81–5.15 (m, 4), 3.02 (br d, 2, J = 6.7, major isomer), 2.61 (br d, 2, J = 6.1, minor isomer), 2.21 (m, 1), 2.09 (m, 1), 1.90 (m, 2), 1.55 (m, 1), 1.45 (m, 1), 0.92 (s, 9, minor isomer), 0.90 (s, 9, major isomer), -0.25 (s, 6, major isomer), -2.06 (s, 6, minor isomer); ^{13}C NMR ($CDCl_3$) 139.2, 138.9, 137.7, 137.0, 129.4, 129.0, 127.8, 127.7, 127.5, 127.4, 118.0, 115.0, 114.20, 114.17, 35.2, 34.1, 33.6, 33.0, 29.8, 28.3, 28.0, 27.1, 25.8, 25.7, -2.9, -4.0.

Reaction of 34a with CAN. A solution of **34a** (100 mg, 0.292 mmol) in 3 mL of CH_3CN was added at rt over 15 min to a solution of CAN (350 mg, 0.638 mmol) and $NaHCO_3$ (100 mg, 1.190 mmol) in 4 mL of CH_3CN. The resulting solution was stirred at rt for 3 h, diluted with 30 mL of ether, and washed with saturated

$NaHCO_3$ solution. The ether layer was dried ($MgSO_4$) and evaporated in vacuo to give 61 mg of a 4.2:1 mixture of **36a** and **38a**. Flash chromatography on silica gel (20:1 hexane–EtOAc) gave 48 mg of an inseparable 4.2:1 mixture of 1-phenyl-2-(2-propenylidene)-6-hepten-1-one (**36a**) and 6,7,8,9-tetrahydro-9-(2-propenyl)-5,9-methanobenzocyclooctene-10(5*H*)-one (**38a**).

The data for **36a**: ^{1}H NMR 7.66 (dd, 2, J = 8.0, 1.5), 7.52 (tt, 1, J = 7.0, 1.5), 7.43 (ddd, 2, J = 8.0, 7.0, 1.5), 6.78 (m, 1), 6.64 (d, 1, J = 11.2), 5.83 (ddt, 1, J = 17.1, 9.1, 7.2), 5.20–5.52 (m, 2), 5.04 (ddt, 1, J = 17.1, 2.1, 7.2), 4.96 (ddt, 1, J = 9.1, 2.1, 1.0), 2.60 (m, 2), 2.10 (m, 2), 1.59 (m, 2); ^{13}C NMR 198.7, 141.5, 141.1, 138.6, 138.2, 132.2, 131.6 129.2, 128.1, 124.6, 114.9, 33.6, 28.5, 26.5.

The data for **38a**: ^{1}H NMR 8.02–8.06 (m, 1), 7.43–7.54 (m, 1), 7.17–7.45 (m, 2), 5.72 (m, 1), 4.90–5.10 (m, 2), 3.22 (m, 1), 2.67 (br dd, 1, J = 13.5, 6.6), 2.29 (br d, 1, J = 13.0), 2.10 (br dd, 1, J = 13.5, 7.9), 1.70 (dd, 1, J = 13.0), 1.00–1.90 (m, 6). The benzylic H at δ 3.22 is coupled to the peaks of the bridging methylene group at δ 2.29 and 1.70.

Synthesis of (Dimethylethyl)dimethyl[(1-phenyl-2-(2-propenyl)-1,6(*Z*)-nonadienyl)oxy]silane (34b). Ketone **33b** (377 mg) was converted to 256 mg (47%) of **34b** and 200 mg (53%) of recovered **33b** as described above for the preparation of **34a**: ^{1}H NMR 7.20–7.35 (m, 5), 5.72–5.95 (m, 1), 5.15–5.44 (m, 2), 4.95–5.15 (m, 2), 3.02 (br d, 1, J = 6.7, major isomer), 2.67 (br d, 1, J = 6.1, minor isomer), 1.80–2.27 (m, 4), 1.25–1.68 (m, 2), 0.92 (s, 9, minor isomer), 0.90 (s, 9, major isomer), 0.85–1.00 (t, 3, CH_3), –0.25 (s, 6, minor isomer), –0.26 (s, 6, major isomer).

Reaction of 34b with CAN. A solution of **34b** (87.5 mg, 0.236 mmol) in 2 mL of CH_3CN was added at rt over 10 min to a solution of CAN (280 mg, 0.511 mmol) and $NaHCO_3$ (80 mg, 0.952 mmol) in 3 mL of CH_3CN, and the reaction mixture was stirred at rt for 3 h. Normal work-up and flash chromatography on silica gel (20:1 hexane–EtOAc) gave 18.6 mg (31%) of 1-phenyl-2-(2-propenylidene)-6(*Z*)-nonen-1-one (**36b**): ^{1}H NMR 7.66 (dd, 2, J = 8.0, 1.5), 7.52 (tt, 1, J = 7.0 1.5), 7.43 (ddd, 2, J = 8.0, 7.0, 1.5), 6.79 (m, 1), 6.63 (d, 1, J = 11.1), 5.27–5.55 (m, 4), 2.61 (m, 2), 1.90–2.20 (m, 4), 1.54 (m, 2), 0.96 (t, 1, J = 7.6); ^{13}C NMR 198.8, 141.3, 132.3, 132.2, 131.6, 129.3, 128.4, 128.1, 124.6, 29.4, 27.1, 26.7, 20.6, 14.3, 2 C not observed; IR (neat) 3060, 2960, 2880, 1725, 1660, 1600, 1580.

Synthesis of (1,1-Dimethylethyl)dimethyl[(1-phenyl-1-(*Z*),6(*Z*),11-dodecatrienyl)oxy]silane (43). Ketone **42** (260 mg, 1.01 mmol) was converted to 360 mg (99%) of an inseparable 5:1 mixture of (*Z*)- and (*E*)-**43** as described in method A: ^{1}H NMR 7.42 (dd, 2, J = 8.1, 1.4), 7.15–7.38 (m, 3), 5.80 (ddt, 1, J = 17.2, 10.0, 6.7), 5.28–5.47 (m, 2), 5.10 (t, 1, J = 7.2), 5.00 (ddt, 1, J = 17.2, 2.1, 1.6), 4.93 (ddt, 1, J = 10.0, 2.1, 1.2), 2.14–2.16 (m, 2), 1.94–2.14 (m, 6), 1.33–1.56 (m, 4), 0.99 (s, 9), 0.91 (s, 9, (*E*)-**43**), 0.03 (s, 6, (*E*)-**43**), –0.05 (s, 6); ^{13}C NMR [(*Z*)-**43**] 149.4, 140.0, 138.5, 130.0, 129.7, 128.0, 127.5, 126.0, 114.5, 111.9, 33.5, 30.0, 29.0, 27.5, 27.0, 26.1, 26.0, 25.9, –4.0; IR (neat) 3070, 2930, 2860, 1655, 1645, 1600, 1580, 745, 685.

Reaction of 43 with Cupric Triflate. A solution of a 5:1 mixture of (*Z*)- and (*E*)-**43** (110 mg, 0.303 mmol) in 2.5 mL of CH_3CN was slowly added over 3 h using a syringe pump to a solution of cupric triflate (360 mg, 0.995 mmol) and Cu_2O (250 mg, 1.75 mmol) in 3 mL of CH_3CN at 25 °C. The solution was stirred at 25 °C for additional 3.5 h and worked up as described above to give 94.1 mg of crude product, which was purified by flash chromatography on silica gel (9:1 hexane–EtOAc) to give 66 mg (80%) of a 4:1 mixture of (3aα,9β,9aβ)-9-(4-pentenyl)-1,2,3,3a,9,9a-hexahydro-4*H*-benz[*f*]inden-4-one (**44**) and (3aα,9α,9aα)-9-(4-pentenyl)-1,2,3,3a,9,9a-hexahydro-4*H*-benz[*f*]-inden-4-one (**45**): ^{1}H NMR 8.03 (ddd, 1, J = 7.9, 7.3, 1.4), 7.90 (ddd, 1, J = 7.9, 9.3, 1.4, **45**), 7.52 (ddd, 1, J = 7.9, 7.3, 1.4), 7.42 (br d, 1, J = 7.9), 7.31 (ddd, 1, J = 7.7, 7.3, 1.6), 5.77 (ddt, 1, J = 17.2, 10.0, 6.7), 5.00 (ddt, 1, J = 17.2, 2.1, 1.6), 4.92 (ddt, 1, J = 10.0, 2.1, 1.2), 2.96 (ddd, 1, J = 10.7, 3.8, 3.8), 2.51 (ddd, 1, J = 13.3, 9.8, 8.0), 0.90–2.35 (m, 13); ^{13}C NMR (**44**) 200.3, 146.6, 138.4, 134.6, 133.1, 127.3, 126.7, 126.2, 114.8, 55.1, 47.4, 45.1, 34.2, 30.8, 30.1, 23.8, 23.3, 22.2; IR (neat) 3035, 2970, 2940, 1690, 1645, 1600, 760, 690. Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.76; H, 8.89.

Synthesis of (1,1-Dimethylethyl)dimethyl[(1-phenyl-1-(*Z*)-hepten-6-ynyl)oxy]silane (56). Ketone **55**[41] (0.373 g, 2.00 mmol) was converted to 0.50 g (83%) of an inseparable 8:1 mixture of (*Z*)- and (*E*)-**56** as described in method A: ^{1}H NMR 7.42 (dd, 2, J = 8.1, 1.4), 7.18–7.32 (m, 3), 5.07 (t, 1, J = 7.2), 5.05 (t, 1, J = 7.2, (*E*)-**56**), 2.26–2.36 (m, 2), 2.24 (dt, 2, J = 2.7, 7.2), 1.95 (t, 1, J = 2.7), 1.66 (t, 1, J = 7.2, (*E*)-**56**), 1.66 (tt, 2, J = 7.2, 7.2), 0.99 (s, 9), 0.91 (s, 9, (*E*)-**56**), 0.03 (s, 6, (*E*)-**56**), –0.05 (s, 6); ^{13}C NMR [(*Z*)-**56**] 150.0, 139.6, 127.9, 127.4, 125.9, 110.5, 84.5, 68.3, 28.6, 25.9, 25.7, 25.3, 18.2, –4.0; IR (neat) 3300, 3030, 2970, 1655, 1600, 1575, 750, 690.

Reaction of 56 with CAN. A solution of **56** (100 mg, 0.33 mmol) in 2.5 mL of CH_3CN was slowly added over 3 h using a syringe pump to a solution of CAN (380 mg, 0.69 mmol) and sodium bicarbonate (120 mg, 1.43 mmol) in 4 mL of CH_3CN at 25 °C. The solution was stirred at 25 °C for additional 3.5 h and worked up as described above to give 320 mg of crude product. Purification by flash chromatography on silica gel (9:1 hexane–ether) gave 4.1 mg of recovered **56**, 12.4 mg of **15** (18%), and 23.4 mg (38%) of acyclic α-nitrooxy ketone **58**.

The data for **58**: ^{1}H NMR 7.95 (dddd, 2, J = 8.1, 1.4, 1.3, 1.0), 7.63 (dddd, 1, J = 7.3, 7.3, 1.4, 1.4), 7.55 (dddd, 2, J = 6.7, 1.5, 1.2, 7.4), 6.10 (dd, 1, J = 9.0, 3.7), 2.30 (dt, 2, J = 2.3, 7.2), 2.11–2.25 (m, 1), 1.95–2.08 (m, 1), 1.97 (d, 1, J = 2.3), 1.75 (tt, 2, J = 7.2, 7.2); ^{13}C NMR 193.9, 134.3, 133.7, 129.1, 128.4, 82.7, 82.0, 69.7, 28.5, 23.4, 14.7; IR (neat) 3305, 3030, 2970, 2930, 1690, 1603, 1585, 1255, 770, 690.

Synthesis of (1,1-Dimethylethyl)dimethyl[(1-phenyl-1-(*Z*)-octen-6-ynyl)oxy]silane (60). Ketone **59** (0.384 g, 1.92 mmol) was converted to 0.54 g (90%) of an 8:1 mixture of (*Z*)- and (*E*)-**60** as described in method A: ^{1}H NMR 7.43 (dd, 2, J = 8.1, 1.4), 7.18–7.32 (m, 3), 5.09 (t, 1, J = 7.2), 5.01 (t, 1, J = 7.2, (*E*)-**60**), 2.23–2.33 (m, 2), 1.78 (t, 3, J = 2.6), 1.74 (t, 3, J = 2.6, (*E*)-**60**), 1.50–1.66 (m, 2), 0.99 (s, 9), 0.91 (s, 9, (*E*)-**60**), 0.03 (s, 6, (*E*)-**60**), –0.05 (s, 6); ^{13}C NMR ($CDCl_3$) [(*Z*)-**60**] 149.8, 139.7, 127.7, 127.4, 125.9, 111.0, 79.2, 75.6, 29.1, 25.9, 25.7, 25.5, 8.6, –4.0; IR (neat) 3060, 2940, 2880, 2240, 1655, 1580, 750, 690.

Reaction of 60 with Cupric Triflate. A solution of an 8:1 mixture of (*Z*)- and (*E*)-**60** (65 mg, 0.21 mmol) in 2.0 mL of CH_3CN was slowly added over 3 h using a syringe pump to a solution of cupric triflate (470 mg, 1.30 mmol), water (10 μl, 0.56 mmol), and Cu_2O (280 mg, 1.96 mmol) in 6 mL of CH_3CN at 25 °C. The solution was stirred at 25 °C for an additional 3.5 h and worked up as described above to give 64.7 mg of crude **64**, which was washed with hexane to give 30 mg (70%) of pure 1,2,3,9-tetrahydro-9-hydroxy-9-methyl-4*H*-benz[*f*]inden-4-one (**64**): mp 175–177 °C (hexane–EtOAc); ^{1}H NMR 8.05 (dd, 1, J = 7.8, 1.4), 7.80 (dd, 1, J = 8.0, 1.4), 7.59 (ddd, 1, J = 8.0, 7.8, 1.4), 7.40 (ddd, 1, J = 7.8, 7.8, 1.4), 2.52–3.02 (m, 4), 1.85–2.15 (m, 2), 1.63 (s, 3); ^{13}C NMR 183.0, 165.8, 149.1, 136.7, 132.6, 130.4, 127.8, 126.3, 126.0, 69.1, 32.7, 29.9, 29.5, 21.6; IR (neat) 3440, 3070, 2970, 2940, 1640, 1600, 1585. Anal. Calcd for $C_{14}H_{14}O$: C, 78.48; H, 6.59. Found: C, 78.13; H, 6.71.

Synthesis of (1*Z*,6*Z*)- and (1*E*,6*Z*)-1-Methoxy-1-phenyl-1,6-nonadiene (65). Montmorillonite K10 clay (3.0 g) in 4 mL of trimethyl orthoformate was stirred for 5 min and filtered to give wet clay.[45] To the wet clay was added a solution of ketone **1a** (639 mg, 2.94 mmol) in 10 mL of pentane, and the reaction mixture was stirred for 16 h. The solution was filtered and the wet clay was washed with 10 mL of pentane. The combined pentane layers were evaporated in vacuo to give 761 mg (99%) of the dimethyl ketal. To a solution of the ketal (600 mg, 2.29 mmol) and *i*-Pr_2NEt (0.6 mL, 3.44 mL) in 5 mL of CH_2Cl_2 at –25 °C was added TMSOTf (0.6 mL, 3.10 mmol) dropwise.[46] The reaction mixture was warmed to rt and stirred for 22 h. The solvent was evaporated, and the residue was washed with petroleum ether (3 × 7 mL). The combined petroleum ether solution was washed with cold saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated in vacuo to give 444 mg of crude **65**, which was purified by flash chromatography on silica gel (hexane) to give 72 mg of a 1:1 mixture of (*Z*)- and (*E*)-**65** and 444 mg of a 1:2 mixture of (*Z*)- and (*E*)-**65** (combined yield 56%). Careful flash chromatography on silica gel (hexane) gave a least polar fraction containing an 8:1 mixture of (*Z*)- and (*E*)-**65**. Replacement of *i*-Pr_2NEt by Et_3N gave a 1:4.2 mixture of (*Z*)- and (*E*)-**65**. Flash chromatography on silica gel (60:1 hexane–ether) gave a most polar fraction containing a 1:10 mixture of (*Z*)- and (*E*)-**65**.

The data for (*Z*)-**65**: ^{1}H NMR 7.46 (dd, 2, J = 8.1, 1.4), 7.22–7.42 (m, 3), 5.30–5.50 (m, 2), 5.32 (t, 1, J = 7.4), 3.53 (s, 3), 2.30 (m,

2), 1.90–2.20 (m, 4), 1.50 (tt, 2, J = 6.0, 6.0), 0.98 (t, 3, J = 7.6); ^{13}C NMR 154.7, 131.9, 128.8, 128.3, 127.6, 127.1, 125.8, 114.5, 58.5, 29.9, 26.9, 25.2, 20.5, 14.3.

The data for (*E*)-**65**: ^{1}H NMR 7.60 (dd, 2, J = 8.1, 1.4), 7.25–7.50 (m, 3), 5.20–5.45 (m, 2), 4.72 (t, 1, J = 7.4), 3.63 (s, 3), 1.90–2.15 (m, 6), 1.50 (tt, 2, J = 6.0, 6.0), 0.93 (s, 3, J = 7.6); ^{13}C NMR 155.3, 136.5, 131.8, 128.9, 128.6, 127.93, 127.90, 100.2, 55.0, 31.3, 27.1, 26.7, 20.5, 14.3; IR (neat) 3030, 2980, 2965, 2930, 1650, 1600, 760.

The stereochemistry is assigned by comparison to the ^{13}C NMR data for the methyl enol ethers of propiophenone[65] and the ^{1}H NMR data for the methyl enol ethers of valerophenone.[66] The methoxy carbon (58.5 vs 55.0) and carbon-2 (114.5 vs 100.2) absorb downfield in the *Z*-isomer. The methoxy hydrogens absorb downfield (3.63 vs 3.53) while hydrogen-2 absorbs upfield (4.72 vs 5.32) in the *E*-isomer.

Reaction of 65 with Cupric Triflate. A solution of an 8:1 mixture of (*Z*)- and (*E*)-**65** (8.8 mg, 0.038 mmol) in 2 mL of CH_3CN was slowly added using a syringe pump to a solution of cupric triflate (35 mg, 0.098 mmol) and cuprous oxide (24 mg, 0.168 mmol) in 1 mL of CH_3CN at rt. The resulting solution was stirred at 25 °C for 2–3 h, diluted with 20 mL of ether, acidified with 5% HCl solution, washed with saturated NaCl solution, dired ($MgSO_4$), and evaporated in vacuo to give 8.0 mg of crude product which was purified by flash chromatography on silica gel (9:1 hexane–EtOAc) to give 60 mg (73%) of an inseparable 7:1 mixture of **5a** and **6a**. A similar reaction with a 1:10 mixture of (*Z*)- and (*E*)-**65** (28 mg, 0.12 mmol) gave 19 mg (74%) of an inseparable 1:7 mixture of **5a** and **6a**.

Synthesis of Trimethyl[(1-phenyl-2-(3-hexenyl)cyclopropyl)]oxy]silane (74). To a solution of **73** (996 mg, 3.63 mmol) and $ZnEt_2$ (1.1 M in toluene, 3.5 mL, 3.85 mmol) in 15 mL of pentane was added dropwise CH_2I_2 (0.6 mL, 7.44 mmol).[59] The reaction mixture was stirred for 20 h, diluted with 50 mL of pentane, washed with cold saturated NH_4Cl solution, dired ($MgSO_4$), and evaporated in vacuo to give 1.11 g of crude **74**, which was purified by flash chromatography on silica gel (hexane) to give 353 mg (31%) of pure **74** as a mixture of isomers: ^{1}H NMR 7.12–7.37 (m, 5), 5.22–5.58 (m, 2), 1.93–2.33 (m, 4), 1.50–2.80 (m, 3), 1.34–1.38 (m, 1), 0.97 (t, 1, J = 7.6, major isomer), 0.85–1.03 (m, 1), 0.76–0.86 (m, 1), 0.09 (s, 9, major isomer); ^{13}C (major isomer) 145.9, 132.0, 129.2, 128.0, 125.8, 124.9, 60.9, 32.5, 28.42, 28.35, 25.6, 20.6, 13.9, 1.1; IR (neat) 3065, 3030, 2980, 2938, 1605. Anal. Calcd for $C_{18}H_{28}OSi$: C, 74.94, H, 9.78. Found: C, 75.02, 9.71.

Reaction of 74 with $Cu(BF_4)_2$. To a solution of $Cu(BF_4)_2$ (500 mg, 2.11 mmol) and Cu_2O (350 mg, 2.45 mmol) in 10 mL of ether was added over 15 min at rt a solution of **74** (292 mg, 1.01 mmol) in 5 mL of ether. The reaction mixture was stirred for 3.5 h, diluted with ether, washed with saturated NH_4Cl solution, washed with saturated $NaHCO_3$ solution, dired ($MgSO_4$), and evaporated in vacuo to give 186 mg of crude **77**, which was purified by flash chromatography on silica gel (hexane–EtOAc, 9:1) to give 46.6 mg (21%, ≈80% pure) of **77**. ^{1}H and ^{13}C NMR spectral and capillary GC analysis (including co-injections with authentic samples) indicated that a 2.5:1 mixture of (*E*)-**77** and (*Z*)-**77** (both as a ≈1:1 cis–trans mixture) was present.

Synthesis of Phenyl[3-(1-propenyl)cyclopent-1-yl]-methanone (77). A solution of norbornene (2.0 g, 21.3 mmol) in 60 mL of 5:1 CH_2Cl_2–MeOH buffered with 0.4 g of $NaHCO_3$ was ozonolyzed at −78 °C (O_3 was bubbled through for about 10 min until the blue color persisted). The solution was purged with N_2 to remove the remaining O_3, filtered, and evaporated in vacuo to give a colorless oil. The residual oil was dissolved in 20 mL of CH_2Cl_2 at 0 °C. Et_3N (6.0 mL, 43.0 mmol) and Ac_2O (2.5 g, 24.5 mmol) were added to the solution successively. The reaction mixture was stirred at rt for 2 days and diluted with ether. The ether solution was washed with 5% HCl solution, washed with saturated NaCl solution, dired ($MgSO_4$), and evaporated in vacuo to give 2.70 g (81%) of a crude 2:3 mixture of *cis*- and *trans*-**78**.[60]

To a suspension of ethyltriphenylphosphonium bromide (3.78 g, 0.2 mmol) in 25 mL of THF was added *n*-BuLi (2.5 M in hexane, 5.0 mL, 12.5 mmol). The reaction mixture was stirred for 10 min and treated with a solution of **78** (1.89 g, 12.1 mmol) in 10 mL of THF. The reaction mixture was heated at 45–50 °C overnight, and 65 mL of 1 N NaOH solution was added. The reaction mixture was heated at reflux for 0.5 h to hydrolyze the ester, cooled to rt, and washed with petroleum ether (3 × 20 mL). The aqueous layer was acidified with 5% HCl solution and extracted with ether (2 × 30 mL). The ether layers were washed with saturated NaCl solution, dired ($MgSO_4$), and evaporated in vacuo to give 626 mg (34%) of **79**: ^{1}H NMR ($CDCl_3$) 11.0 (br, 1 CO_2H), 5.20–5.55 (m, 2), 2.70–3.05 (m, 2), 1.20–2.40 (m, 6), 1.60–1.66 (m, 2 allylic CH_3).

A solution of PhLi (1.8 M, 5.0 mL, 9.0 mmol) in 7:3 cyclohexane–ether was added to a solution of **79** (626 mg, 4.06 mmol) in 30 mL of ether at 0 °C. The reaction mixture was stirred for 2 h, acidified with 5% HCl solution, washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated in vacuo to give 584 mg of crude product which was purified by flash chromatography on silica gel (20:1 hexane–EtOAc) to give 250 mg (30%) of a 2:1 mixture of (*Z*)-**77** and (*E*)-**77**. (*Z*)-**77** was a 3:4 mixture of stereoisomers.

A solution of the above mixture (100 mg, 0.047 mmol) and *p*-toluenesulfinic acid (100 mg, obtained from acidification of the commercially available sodium salt) in 10 mL of dioxane was heated at reflux for 3.5 h, cooled to rt, and diluted with 50 mL of ether.[47] The ether solution was washed with 1 N NaOH solution, washed with saturated NaCl solution, dired ($MgSO_4$), and evaporated in vacuo to give 120 mg of crude product which was purified by flash chromatography on silica gel (20:1 hexane–EtOAc) to give 95 mg (95%) of a 1:4 mixture of (*Z*)- and (*E*)-**77**, (*E*)-**77** was a 2:3 mixture of stereoisomers.

The data for a 3:4 mixture of stereoisomers of (*Z*)-**77**: ^{1}H NMR 7.96 (dddd, 2, J = 7.0, 1.5, 1.3, 1.0), 7.55 (dddd, 1, J = 7.3, 7.3, 1.5, 1.3), 7.46 (dddd, 2, J = 7.3, 7.0, 1.5, 1.3), 5.13–5.60 (m, 2), 3.66–3.92 (m, 1), 2.83–3.03 (m, 1), 1.78–2.25 (m, 4), 1.65 (m, 3, allylic methyl), 1.58–1.78 (m, 1), 1.36–1.55 (m, 1); ^{13}C NMR 202.4, 202.2, 136.9 (ipso), 136.7 (ipso), 134.5, 134.4, 132.7 (para), 128.4 (ortho, meta), 123.6, 123.3, 46.3, 45.6, 38.7, 37.4, 37.2, 36.7, 34.1, 33.1, 29.4, 29.2, 13.1, 13.0; IR (neat) 3030, 2975, 2860, 1683, 1600, 1580.

The data for a 2:3 mixture of stereoisomers of (*E*)-**77**: ^{1}H NMR 7.96 (dddd, 2, J = 7.0, 1.5, 1.3, 1.0), 7.55 (dddd, 1, J = 7.3, 7.3, 1.5, 1.3), 7.46 (dddd, 2, J = 7.3, 7.0, 1.5, 1.3), 5.25–5.65 (m, 2), 3.66–2.93 (m, 1), 2.47–2.67 (m, 1), 1.78–2.20 (m, 4), 1.65 (m, 3, allylic methyl), 1.58–1.78 (m, 1), 1.36–1.55 (m, 1); ^{13}C NMR 202.5, 202.3, 137.0 (ipso), 136.8 (ipso), 134.7, 134.6, 132.7 (para), 128.5 (ortho, meta), 123.9, 123.8, 46.2, 45.4, 44.3, 42.6, 37.0, 36.3, 33.6, 32.9, 29.1, 29.0, 17.92, 17.86; IR (neat) 3030, 2975, 2860, 1683, 1600, 1580.

Capillary GC on Alltech RSL 150 (60 °C to 150 °C at 10 °C/min, 150 °C for 5 min, 20 °C/min to 190 °C, and 190 °C for 10 min) resolved the four isomers into three peaks: t_R = 14.6 and 15.1 min for (*Z*)-**77** and t_R = 14.9 min for (*E*)-**77**.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for compounds **33b**, **34b**, **36a**, **36b**, **42**, **56**, **58**, **59**, **60**, (*Z*)-**65**, (*E*)-**65**, and **77** (from **74** and **79**) (26 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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