Regiospecific Synthesis of β,γ-Unsaturated Ketones from Allylic Alcohols. Claisen Rearrangement of α-Allyloxy Ketone Enol Derivatives

Joseph L. C. Kachinsky and Robert G. Salomon*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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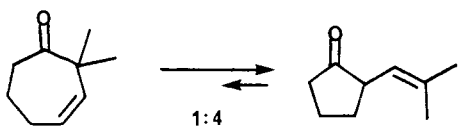
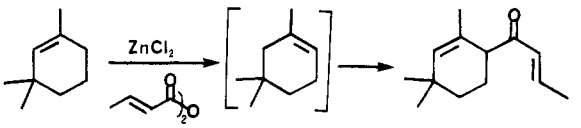
β,γ-Unsaturated ketones are prepared with regiospecific C–C bond formation at the former γ-position of primary, secondary, or tertiary allylic alcohol precursors by a process involving [3.3] sigmatropic Claisen rearrangement of intermediate α-allyloxy ketone enolates or the corresponding trimethylsilyl enol ethers. Although enolates of α-allyloxy ketones might be intermediates, byproducts from competing [1.2] or [2.3] sigmatropic rearrangements of α-allyloxy enolates are not found.

Synthesis of β,γ-unsaturated ketones is complicated, inter alia, by a proclivity toward prototropic rearrangement producing conjugated isomeric α,β-unsaturated ketones.[1] Although deconjugation of α,β-unsaturated ketones can be achieved by a variety of methods,[2] mixtures of α,β- and β,γ-unsaturated isomers are often produced. Photoenolization allows contrathermodynamically complete deconjugation. However, the product β,γ-unsaturated ketones may undergo further photorearrangements such as 1,3-acyl shift.[3] The latter rearrangement provides a novel synthesis of certain β,γ-unsaturated ketones from other β,γ-unsaturated ketones.[4] However, isomeric mixtures are usually produced as in the example of eq 1,[2d] and a wide



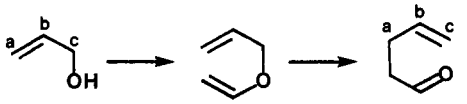
(1)

variety of other photoproducts may be generated, e.g. by α-cleavage, γ-hydrogen abstraction, or di-π-methane rearrangement of β,γ-unsaturated ketones. Some C–C connective methods for synthesis of β,γ-unsaturated ketones have similar shortcomings. Acylation of olefins frequently favors the production of β,γ-unsaturated ketones, but α,β-unsaturated isomers may also be generated.[5] Further ambiguity may complicate preparative applications of this method. To wit, olefin isomerization may occur under the acylation reaction conditions leading to unexpected products as in the example of eq 2.[6]



(2)

A general method for unambigious synthesis of β,γ-unsaturated ketones from allylic alcohols **1** would be especially valuable since these precursors are readily available. However, possible reaction with or without allylic rearrangement often precludes regiospecificity for syntheses involving allylic reactants. Thus, alkylation of enolate nucleophiles with allylic electrophiles delivers γ,δ-unsaturated carbonyl compounds **3** nonregiospecifically. An alternative strategy provides a regiospecific method for C–C connective synthesis of γ,δ-unsaturated carbonyl compounds **3** from allylic alcohols **1** by exploiting Claisen rearrangement of intermediate allyl vinyl ethers **2** (eq 3).[7] Owing to a pericyclic mechanism, this rearrangement allows a stereo- and regiospecific C–C bond formation with 1,3-transfer of chirality accompanying α-(acylalkyl)-dehydroxy substitution.[8]



1 **2** **3** (3)

Synthesis of β,γ-unsaturated carbonyl compounds **4** from allylic alcohols **1** is more difficult. The usual electrophilic reactivity of a carbonyl carbon must first be inverted for a polar C–C bond formation with allylic electrophiles (eq 4).[9,10] Moreover, competing S_N2 and S_N2'

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(3) Carlson, R. G.; Bateman, J. H. *Tetrahedron Lett.* **1967**, 4151.

(4) (a) Keifer, E. F.; Carlson, D. A. *Tetrahedron Lett.* **1967**, 1617. (b) Paquette, L. A.; Eizember, R. F.; Cox, O. *J. Am. Chem. Soc.* **1968**, *90*, 5153. (c) Dauben, W. G.; Kellog, M. S.; Seeman, J. I.; Spitzer, W. A. *Ibid.* **1970**, *92*, 1786. (d) Engel, P. S.; Schexnayder, M. A. *Ibid.* **1972**, *94*, 9252. (e) Schexnayder, M. A.; Engel, P. S. *Ibid.* **1975**, *97*, 4825. (f) Dauben, W. G.; Lodder, G.; Robbins, J. D. *Ibid.* **1976**, *98*, 3030. (g) Schafner, K. *Tetrahedron* **1976**, *32*, 641.

(5) (a) Deno, N. C.; Chafetz, H. *J. Am. Chem. Soc.* **1952**, *74*, 3940. (b) Groves, J. K.; Jones, N. *J. Chem. Soc. C* **1968**, 2215, 2898. Dufort, N.; Lafontaine, J. *Can. J. Chem.* **1968**, *46*, 1065. (c) Groves, J. K.; Jones, N. *J. Chem. Soc. C* **1969**, 608. (d) Vandewalle, M.; Morizur, J.-P.; Furth, B. *Bull. Soc. Chim. Fr.* **1970**, 2027. (e) Smit, W. A.; Semenovsky, A. V.; Kucherov, V. F.; Chernova, T. N.; Krimer, M. Z.; Lubinskoya, O. V. *Tetrahedron Lett.* **1971**, 3101. (f) Smit, V. A.; Semenovskii, A. V.; Lybinskaya, O. V.; Kucherov, V. F. *Dokl. Akad. Nauk SSSR Engl. Transl.* **1972**, *203*, 272. (g) Adams, D. R.; Bhatnager, S. P.; Cookson, R. C.; Tuddenham, R. M. *Tetrahedron Lett.* **1974**, 3903. (h) Monti, S. A.; White, G. L. *J. Org. Chem.* **1975**, *40*, 215. (i) Hoffman, H. M. R.; Tsushima, T. *J. Am. Chem. Soc.* **1977**, *99*, 6008. (j) Beak, P.; Berger, K. R. *Ibid.* **1980**, *102*, 3848.

(6) (a) Groves, J. K.; Jones, N. *Tetrahedron Lett.* **1970**, 1161. (b) Klein, E.; Rojahn, W. *Ibid.* **1971**, 3607.

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(8) For IUPAC nomenclature for transformations see: Bunnett, J. F. *Pure. Appl. Chem.* **1981**, *53*, 305.

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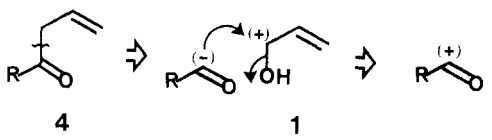
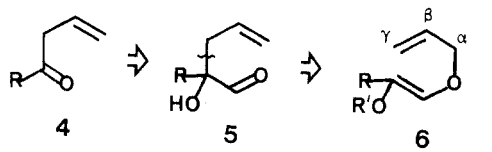


4 1 (4)

processes complicate regiocontrol during allylation of acyl nucleophiles, i.e. "acyl carbanion equivalents".[11] We conceived an alternative approach wherein β,γ-unsaturated ketones **4** are prepared from allylic alcohols **1** by exploiting Claisen rearrangements. Our strategy (eq 5) presumes that



4 5 6 (5)

the target ketones **4** can be generated by oxidative cleavage of α-hydroxy aldehydes **5** available, in turn, by Claisen rearrangement of enol ethers **6**. The practical utility of this strategy depends on the availability of β-(allyloxy)vinyl ethers **6** from allyl alcohols **1**.

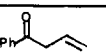
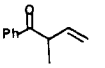
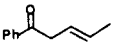
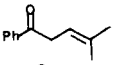
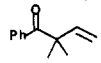
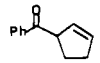
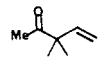
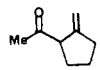
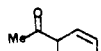
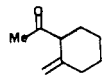
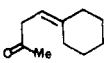
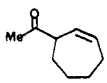
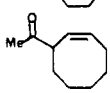
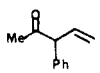
We now report that silyl enol ethers **6** (R′ = $SiMe_3$) apparently are readily available from the corresponding α-allyloxy ketones **7**, but undergo Claisen rearrangement even under the mild conditions which we employed for their formation. Most importantly, the resulting α-hydroxy γ,δ-unsaturated aldehydes **5** can be converted into allyl ketones **4** without accompanying formation of the corresponding vinyl ketones. Of course the new C–C bond is formed specifically at the former γ-position of the allylic alcohol precursor.

Results and Discussion

Synthesis of Allyloxy Ketones. Several methods were examined for conversion of allylic alcohols **1** into α-allyloxy ketones **7** (Table I). BF_3-catalyzed reaction of diazoacetophenone with allylic primary alcohols provides the corresponding phenacyl ethers **7a,b,e** in excellent yields (79–93%).[12] However, inferior results were obtained with more highly α-substituted allylic alcohols, presumably owing to their proclivity toward acid-catalyzed decomposition via allylic carbocations.

Allylic primary, secondary, and tertiary alcohols were transformed into the corresponding α-allyloxy ketones by a two-step process involving alkylation with epoxides, i.e. styrene oxide or propylene oxide. Subsequent oxidation of the intermediate β-allyloxy alcohols,[13] e.g. **8**, with pyridinium chlorochromate (PCC)[14] afforded the desired α-allyloxy ketones **7c,d,f,g**. Another route to α-allyloxy ketones was briefly examined. Thus, reaction of methylmagnesium iodide with α-(allyloxy)acetonitriles **9** provided **7g** and **7p**. This approach should be applicable to the synthesis of a wide variety of α-allyloxy ketones **7** and the derived (vide infra) β,γ-unsaturated ketones **4** from Grignard reagents **10**.

Table I. Regiospecific Synthesis of Allyl Ketones 4 from Allylic Alcohols 1

Entry	Allylic Alcohol 1	Method[a]	Allyloxy Ketone 7 Yield (%)	α-Silyloxy Aldehyde 14 Yield (%)	Allyl Ketone 4	Ketone 4 Yield (%)
a		A	79	85		95
b		A	90	98		83
c		B	40	85		79
d		B	28	99		81
e		A	93	99		83
f		B	30	80		93
g		C	62	90		80
h		D	83	88		63
i		D	95	84		72
j		D	73	84		91
k		D	95	95		81
m		D	95	92		84
n		D	95	91		98
o		D	87	89		94

[a] Method A, $PhCOCHN_2/BF_3{\cdot}OEt_2$; method B, NaH then $PhCHOCH_2$ and PCC; method C, NaH then $MeCHOCH_2$ and PCC; method D, $CH_2{=}C(OMe)CH_2Br$ then 1 N HCl.

(9) For reviews see: Seebach, D. *Synthesis* **1969**, 17. Grobel, B.-T.; Seebach, D. *Ibid.* **1977**, 357.

(10) (a) Of course allylic electrophiles may be converted into nucleophiles, e.g. organometallics, that often provide β,γ-unsaturated ketones *regioselectively* by acylation[10b-j] or alkylation with aldehydes[10k] followed by oxidation of the resulting homoallylic alcohols.[10l] However, this strategy generally does *not* provide a *regiospecific* route from allylic electrophiles to β,γ-unsaturated ketones. (b) Allylic magnesium halides with nitriles: Andrac, M. *Ann. Chim. (Paris)* **1964**, *9*, 287. Kergomard, A.; Veschambre, H. *Tetrahedron Lett.* **1976**, 4069. (c) Allylboranes with alkoxyacetylenes: Mikhailov, B. M.; Bubnov, Y. N.; Korobeinikova, S. A.; Frolov, S. I. *J. Organomet. Chem.* **1971**, *27*, 165. Mikhailov, B. M.; Bubnov, Y. M.; Grigoryan, M. S. *J. Gen. Chem. USSR (Engl. Transl.)* **1974**, *44*, 2425. Bubnov, Y. N.; Lavrinovich, L. I. *Tetrahedron Lett.* **1985**, *26*, 4551. (d) Allylic silanes with acyl halides: Calas, R.; Dunogues, J.; Pillot, J.-P.; Biran, C.; Pisciotti, F.; Arreguy, B. *J. Organomet. Chem.* **1975**, *85*, 149. Pillot, J.-P.; Dunogues, J.; Calas, R. *Tetrahedron Lett.* **1976**, 1871. Ojima, I.; Kumagai, M.; Miyazawa, Y. *Ibid.* **1977**, 1385. (e) Allylic stannanes with acyl halides: Kosugi, M.; Shimizu, Y.; Migata, T. *J. Organomet. Chem.* **1977**, *129*, C36. (f) Allylic magnesium halides with dithioesters: Masson, S.; Saquet, M.; Thuillier, A. *Tetrahedron* **1977**, *33*, 2949. Gosselin, P.; Masson, S.; Thuillier, A. *Tetrahedron Lett.* **1978**, 2717. Gosselin, P.; Masson, S.; Thuillier, A. *J. Org. Chem.* **1979**, *44*, 2807. (g) Allylic mercurials with acyl halides: Hanusa, L. H. *Diss. Abstr. B* **1979**, *39*, 5378. (h) Allylic manganous chlorides and carboxylic acid anhydrides: Cahiez, G.; Alexakis, A.; Normant, J. F. *Synth. Commun.* **1979**, *9*, 639. (i) Allylnickel halides with 2-pyridyl carboxylates: Onaka, M.; Goto, T.; Mukaiyama, T. *Chem. Lett.* **1979**, 1483. (j) Allylic zinc halides with nitriles: Rousseau, G.; Conia, J. M. *Tetrahedron Lett.* **1981**, *22*, 649. (k) Gibson, T. W.; Erman, W. F. *J. Org. Chem.* **1972**, *37*, 1148. (l) Bond, F. T.; Jones, H. L.; Scerbo, L. *Tetrahedron Lett.* **1965**, 4685. Ranganathan, S.; Ranganathan, D.; Mehrotra, M. M. *Synthesis* **1977**, 838. Servin, M.; Krief, A. *Tetrahedron Lett.* **1978**, 187.

(11) (a) Metallated dithioacetals: Reece, C. A.; Rodin, J. O.; Brownlee, R. G.; Duncan, W. G.; Silverstein, R. M. *Tetrahedron* **1968**, *24*, 4249. Hoppmann, A.; Weyerstahl, P. *Ibid.* **1978**, *34*, 1723. (b) Metallated vinyl ethers: Baldwin, J. E.; Hölfe, G. A.; Lever, O. W., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7126. Boeckman, R. K., Jr.; Bruza, K. J.; Baldwin, J. E.; Lever, O. W., Jr. *J. Chem. Soc., Chem. Commun.* **1975**, 519. (c) Metalated α-(trimethylsilyl)oxy nitriles: Hunig, S.; Wehner, G. *Synthesis* **1975**, 180.

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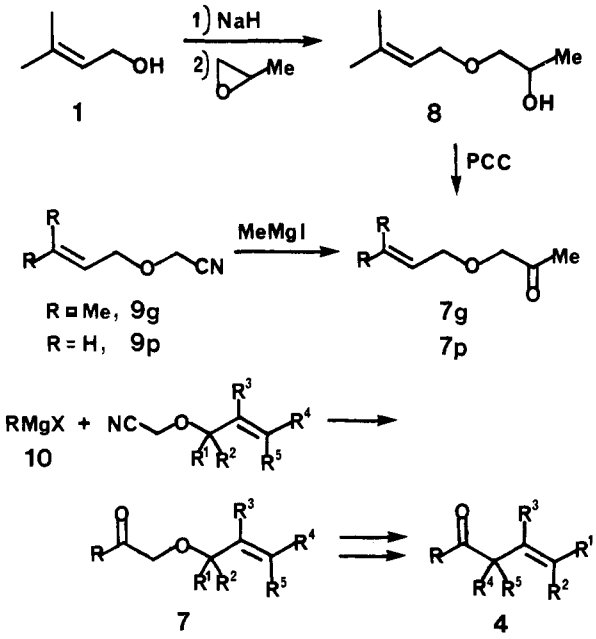
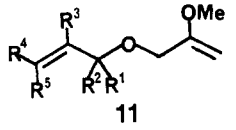
(13) (a) Swern, D.; Billen, G. N.; Knight, H. B. *J. Am. Chem. Soc.* **1949**, *71*, 1152. (b) Kaelin, A. *Helv. Chim. Acta* **1947**, *30*, 2132. (c) Chitwood, H. C.; Freure, B. T. *J. Am. Chem. Soc.* **1946**, *68*, 680.

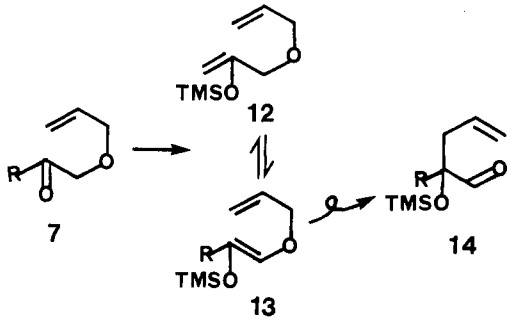
(14) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.



Finally, the reaction of allylic alkoxides with 2-methoxyallyl bromide[15] followed by acid-catalyzed hydrolysis of the intermediate enol ethers **11** provided acetonyl allyl ethers in excellent overall yields from primary, secondary, or tertiary allylic alcohols **1** (Table I).



Claisen Rearrangement of α-Allyloxy Ketone Trimethylsilyl Enol Ethers. Conversion of the allyloxy ketones **7** into allyl vinyl ether substrates for Claisen rearrangement requires enol etherification. Enol silylation of acetonyl ethers **7g–o** could generate both diallyl ethers **12** and the desired allyl vinyl ethers **13**. We therefore

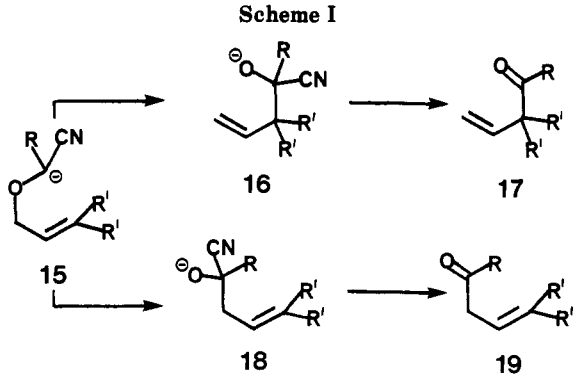


employed enol silylation reaction conditions, which are known to equilibrate the enol ether products: boiling under reflux with chlorotrimethylsilane and triethylamine in dimethylformamide.[16] We anticipated that in situ Claisen rearrangement of **13** would drive this equilibrium toward the desired product. In fact, α-[(trimethylsilyl)oxy] aldehydes **14** are produced from allyloxy ketones **7** in excellent yields (84–98%) under these reaction conditions (Table I).

(15) (a) Prepared from 2-methoxypropene[15b] by reaction with *N*-bromosuccinimide. Minor amounts of 2-methoxy-1-bromopropene are also produced, but this contaminant does not interfere with the desired reaction: Greenwood, G.; Hoffmann, H. M. R. *J. Org. Chem.* **1972**, *37*, 611. See also: Jacobson, R. M.; Raths, R. A.; McDonald, J. H. *Ibid.* **1977**, *42*, 2545. Horning, D. E., Kavadias, G.; Muchowski, J. M. *Can. J. Chem.* **1970**, *48*, 975. (b) Newman, M. S.; Vander Zwan, M. C. *J. Org. Chem.* **1973**, *38*, 2910.

(16) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

Scheme I



Scheme II

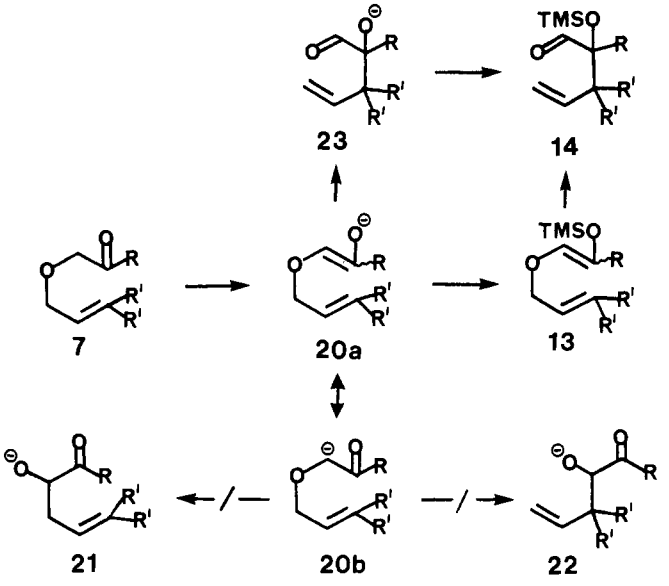


Table II. Oxidation of 2-Phenyl-2-(trimethylsiloxy)-4-pentenal (14a)

method[a]	reactn time, h	yield,[c] %	method[a]	reactn time, h	yield,[c] %
1 (1.0)[b]	16	86	2 (1.2)	1.0	95
1 (2.0)	9	76	2 (1.2)	3.0	91
1 (3.0)	6	60[d]	3 (2.0)	3	53 (48)[e]
2 (1.2)	0.25	96			

[a] Method 1, acetone, CrO_3, H_2O, H_2SO_4, 5 °C; method 2, methanol, H_2O, boil under reflux, then HIO_4, 25 °C; method 3, $NaIO_4$, HOAc, acetone, 40 °C, 100 μL (0.43 mmol) silyloxy aldehyde (**14a**). [b] Molar equivalents of oxidant. [c] Based on NMR internal standard. [d] Prehydrolyzed. [e] Unoxidized silyloxy aldehyde.

The ^1H NMR spectra of the α-phenyl-α-[(trimethylsilyl)oxy] aldehydes **14** (R = Ph) exhibit characteristic absorptions for the α-[(trimethylsilyl)oxy], β-allylic, and aldehydic protons at δ 0.14–0.20, 2.77–3.50, and 9.50–9.78, respectively. The ^1H NMR spectra of the α-methyl-α-[(trimethylsilyl)oxy] aldehydes **14** (R = Me) exhibit similar absorptions at δ 0.10–0.15, 2.3–2.9, and 9.37–9.62 for the respective groups. Two chiral centers are generated during rearrangement of some allyloxy ketones **7**. In most cases ^1H NMR analysis of the product silyloxy aldehydes **14** (**i.e., b, h, j, n,** and **o**) shows diastereomeric mixtures ranging from 30:70 to 50:50 (see the Experimental Section). However, separation of these diastereomers is unnecessary since both afford the same allyl ketone **4**.

The high yields of α-[(trimethylsilyloxy)] aldehydes **14** produced from allyloxy ketones **7** are remarkable. Several alternative rearrangements might have been expected to compete with the desired [3.3] sigmatropic Claisen rearrangement. In this connection it is noteworthy that α-

allyloxy carbanions **15** from α-(allyloxy)acetonitriles undergo mainly [2.3] sigmatropic rearrangement leading to 1,3-transposed allyl ketones **17** via α-cyano alkoxides **16**[17] at −78 °C (Scheme I). Minor amounts of untransposed allyl ketones **19** derived from α-cyano alkoxides **18** are also produced at this temperature. At higher temperatures the [1.2] sigmatropic rearrangement of **15** to **18** predominates over the [2.3] sigmatropic rearrangement of **15** to **16**. The generation of aldehydes **14** from allyloxy ketones **7** might involve enolate intermediates **20b** (Scheme II) closely analogous to the α-allyloxy carbanions **15** (Scheme I). Yet the well-known [1.2] or [2.3] sigmatropic rearrangements of such carbanions,[17,18] which might produce **21** or **22**, respectively, from **20b**, did not occur. If enolates **20** are intermediates, either silylation to give **13** is much faster than rearrangements to **21** or **22**, or the enolates themselves undergo Claisen rearrangement (i.e., **20a** to **23**) in preference to other sigmatropic rearrangements.[18f] Alternatively, the enolates **20** may not be intermediates in the enol silylation of α-allyloxy ketones **7** under the reaction conditions that we employed.

Oxidative Cleavage of γ,δ-Unsaturated α-Silyloxy Aldehydes. Several reagents and reaction conditions were explored for conversion of 2-phenyl-2-[(trimethylsilyl)-oxy]-4-pentenal (**14a**) into 1-phenyl-3-buten-1-one (**4a**) (Table II). Treatment of a solution of silyloxy aldehyde **14a** in acetone with 1.75 M CrO_3 in aqueous H_2SO_4 (method 1) afforded allyl ketone **4a** presumably via preliminary acid-catalyzed hydrolysis to the α-hydroxy aldehyde. With 1 equiv of oxidant, complete consumption of **14a** required 16 h. The β,γ-unsaturated ketone **4a** was obtained in good yield (86%) uncontaminated with the corresponding α,β-unsaturated ketone. With 2 or 3 equiv of oxidant, shorter reaction times were adequate, but yields were also lower. Hydrolysis of the silyloxy aldehyde **14a** to hydroxy aldehyde **5a** was slow in aqueous methanolic periodic acid at room temperature. Consequently, the conversion of **14a** to the β,γ-unsaturated ketone **4a** was inefficient under these conditions. Therefore, the silyloxy aldehyde was prehydrolyzed by boiling under reflux in aqueous methanolic solution. Subsequent addition of periodic acid (method 2) resulted in rapid (15-min) conversion to **4a** in excellent yield (96%). Prolonged reaction times did not destroy the product or cause isomerization to the α,β-unsaturated ketone. However, impurities in the crude product were sometimes evident, owing to the appearance of a pink coloration, and these impurities catalyzed isomerization of the β,γ- to the α,β-unsaturated ketone. Fluorescent room lights apparently promote this decomposition (see the Experimental Section). Conversion of **14a** into ketone **4a** by reaction with aqueous sodium periodate in acetic acid and acetone (method 3) at 40 °C was especially mild. However, completion of the process required long reaction times, owing to slow hydrolysis of **14a** under these conditions. Generally, a two-step, one-pot hydrolysis–oxidation with periodic acid was most effective for conversion of α-silyloxy aldehydes **14** into the corresponding β,γ-unsaturated ketones **4**.

C–C Connective Synthesis of β,γ-Unsaturated Ketones. The difficulties associated with exploiting acylation of allylic nucleophiles or allylation of acyl carbanion equivalents for regiospecific preparation of β,γ-unsaturated ketones from allylic alcohols were considered in the introduction. Topologically different C–C connective strategies[19] that avoid the ambiguities engendered by allylic reactants generally provide specific β,γ-unsaturated ketones.[20] Nevertheless, allylic alcohols remain attractive starting materials since they are readily available. The regiospecificity and scope of our new C–C connective synthesis of β,γ-unsaturated ketones **4** from allylic alcohols **1** is nicely demonstrated by the conversions of **1b–e** into **4b–e**, respectively (see Table I). The method is applicable to primary, secondary, and tertiary allylic alcohols. Previously, allylic alcohols have been converted to β,γ-unsaturated ketones with regiospecific C–C bond formation at the former α-position of the allylic alcohol precursor by a process involving two consecutive [3.3] sigmatropic rearrangements.[21] Our new synthetic method, which results in C–C bond formation at the former γ-position of the allylic alcohol precursor, complements this and other methods that generate β,γ-unsaturated ketones or aldehydes via molecular rearrangements.[17,22]

Experimental Section

Analytical Procedures. Preparative gas–liquid phase chromatography (GLPC) of reaction products for spectral identification was performed on a Case Institute constructed instrument equipped with a thermal conductivity detector (TCD). Analytical GLPC was done on either a Varian 1200 or 100 instrument equipped with a flame ionization detector (FID). GLPC columns used: A, 3 ft × $^1/_4$ in. 5% SE 30 on 60/80 Chromosorb G (DMCS-AW); B, 5 ft × $^1/_4$ in. 20% SE 30 on 60/80 Chromosorb P; C, 5 ft × $^1/_4$ in. 15% FFAP on 60/80 Chromosorb P (NAW); D, 3 ft × $^1/_8$ in. 10% DC 710 on 80/100 Chromosorb W (AW);

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E, 5 ft × 1/8 in. 10% SE 30 on 80/100 Chromosorb P (stainless-steel tubing); F, 5 ft × 1/8 in. 10% FFAP on Chromosorb P; G, 5 ft × 1/4 in. 5% FFAP on 60/80 Chromosorb G. Preparative and analytical thin-layer chromatography (TLC) was accomplished on precoated TLC plates (ca. 9-cm length), silica gel 60F-254, layer thickness 0.50 and 0.25 mm, respectively, manufactured by E. Merck and Co., using chloroform (Spectrograde) as the developing solvent unless otherwise specified. Nuclear magnetic resonance (^{1}H NMR) spectra were taken of solutions in deuteriochloroform ($CDCl_3$) unless otherwise noted and recorded on a Varian A-60 or HA-100 spectrometer. Chemical shifts are reported in δ units relative to internal tetramethylsilane (Me_4Si). Mass spectra (MS) were obtained on a DuPont 21-490 gas chromatograph/mass spectrometer (GC/MS) system equipped with a 21-094 Data System using either the direct (batch) inlet, as specified, or, generally, the GLPC inlet (injection port, 180 °C; column temperature, as specified; detector, 200 °C). All spectra were run at an ionization voltage of 70 eV (300 mA) unless otherwise noted and values in parentheses are the relative intensities of the peaks.

Reagents. Allylic alcohols were purchased from Aldrich Chemical Co. or Chemical Samples Co. and used as received. "Dry" solvents were dried immediately prior to use. Benzene and tetrahydrofuran (THF) were distilled from the blue potassium ketyl of benzophenone. Diethyl ether was distilled from lithium aluminum hydride (LAH). Pentane and triethylamine were distilled from calcium hydride. Methylene chloride (CH_2Cl_2) was dried by stirring over phosphorus pentoxide, followed by distillation and storage over molecular sieves (3A). Hexamethylphosphoramide (HMPA) and trimethylchlorosilane (Me_3SiCl) were used as received from Aldrich Chemical Co. Chloroform was Spectrograde quality. Sodium periodate ($NaIO_4$) and periodic acid ($HIO_4 \cdot 2H_2O$) were analytical or analyzed reagent grade. Florisil (60/100 mesh) was used as received from Fisher Scientific Co. Pyridinium chlorochromate (PCC) obtained from Aldrich Chemical Co. was dried in an oven (110 °C) for several hours and allowed to cool under high vacuum (0.5 mm). The reagents 2-methoxyallyl bromide[15] and diazoacetophenone[12,23] were prepared as described previously. All other solvents and reagents were analytical, reagent, or Spectrograde quality unless otherwise noted.

Allyl Phenacyl Ether [α-(Allyloxy)acetophenone, 7a].[12] To a flame-dried 100-mL round-bottom flask equipped with a condenser and containing diazoacetophenone (2.0 g, 13.7 mmol), allyl alcohol (10 mL, 146 mmol), and anhydrous ethyl ether (50 mL) was added $BF_3 \cdot Et_2O$ (50 μL) via syringe. The resulting yellow solution was magnetically stirred under nitrogen for 3–4 h at room temperature. Nitrogen evolution was barely visible 1 h after the addition of $BF_3 \cdot Et_2O$. The reaction mixture was concentrated to ca. 25 mL on steam bath, washed with H_2O (20 mL), aqueous $NaHCO_3$ (50% saturated, 2 × 20 mL), and, aqueous saturated NaCl (2 × 20 mL), and dried (Na_2SO_4). Solvent was removed via rotary evaporation in vacuo and the remaining liquid distilled under reduced pressure to yield **7a**: 2.41 g (79%); bp 112–116 °C (3.5 mm) [lit.[12] bp 130–143 °C (14 mm)]; NMR δ 4.12 (complex d, 2 H, J = 5 Hz), 4.70 (s, 2 H), 5.0–5.5 (m, 2 H), 5.6–6.3 (m, H), 7.2–7.6 (m, 3 H), 7.8–8.0 (m, 2 H); MS, m/e 176 (1), 120 (56), 105 (100), 77 (56), 51 (18), 41 (22).

The phenacyl ethers **7b** and **7e** were prepared similarly:

2-Butenyl Phenacyl Ether [(Crotyloxy)acetophenone, 7b]: 90% yield; bp 104–110 °C (0.9–1.0 mm); NMR δ 1.72 (m, 3 H), 4.12 (m, 2 H), 4.72 (2 H), 5.57–5.88 (2 H), 7.27–7.67 (3 H), 7.96 (m, 2 H); MS, m/e 190 (1), 120 (88), 105 (100), 77 (54), 55 (37), 51 (15).

3-Methyl-2-butenyl Phenacyl Ether [(Prenyloxy)acetophenone, 7e]: 93% yield; bp 120–125 °C (1 mm); NMR δ 1.68 (s, 3 H), 1.75 (s, 3 H), 4.12 (d, 2 H, J = 7 Hz), 4.68 (s, 2 H), 5.40 (complex t, H, J = 7 Hz), 7.2–7.6 (m, 3 H), 7.8–8.1 (m, 2 H); MS, m/e 204 (1), 120 (77), 105 (100), 85 (11), 77 (32), 69 (20), 41 (24).

2-(3-Butenyl) Phenacyl Ether [[(1-Methylallyl)oxy]acetophenone, 7c]. To a flame dried, three-neck 250-mL Morton flask, equipped with a mechanical stirrer and condenser, was added NaH (4.63 g, 0.11 mol, 57% dispersion in oil) that was washed once with dry pentane (50 mL). THF (100 mL) and HMPA (50 mL) were introduced, and 3-buten-2-ol (97%, 7.40 g, 0.10 mol) was added dropwise over a 30-min period under dry nitrogen. The resulting yellowish solution was refluxed for 3 h and cooled to room temperature, and styrene oxide (11.5 mL, 12.0 g, 0.10 mol) was added dropwise over 15–20 min. After 30 min of stirring at room temperature, the mixture was boiled under reflux for 4 h. The cooled reaction mixture was quenched with H_2O (50 mL), acidified with aqueous 3 N HCl, and extracted with ether (5 × 50 mL). The extracts were combined, washed with H_2O (3 × 20 mL), aqueous $NaHCO_3$ (50% saturated, 2 × 20 mL), and aqueous saturated NaCl (2 × 50 mL), and finally dried (Na_2SO_4). The solvent was removed via rotary evaporation in vacuo and the remaining liquid distilled over a short path to yield 10.4 g (54%) of *[(1-methylallyl)oxy]-2-phenylethanol*: bp 86–95 °C (0.5–0.6 mm); NMR δ 1.28 (d, 3 H, J = 6 Hz), 2.78 (s, H), 3.2–4.1 (3 H), 4.7–4.9 (complex d, H), 4.9–5.3 (2 H), 5.6–6.0 (complex dd, H, J = 17, 9 Hz), 7.30, 7.32 (2 s, 5 H); MS, m/e 192 (1), 137 (19), 108 (14), 107 (100), 79 (29), 77 (14), 55 (22).

To a mechanically stirred orange suspension of pyridinium chlorochromate[14] (PCC; 98%, 4.4 g, 20 mmol) in dry CH_2Cl_2 (30 mL) was added a solution of the above [(methylallyl)oxy]-phenylethanol (1.92 g, 10 mmol) in CH_2Cl_2 (10 mL) via syringe. The solution turned black after a few seconds, depositing the reduced reagent on the bottom of the flask. After 4 h, dry ether (50 mL) was added and stirring continued 15 min. The reaction mixture was then poured into a 250-mL beaker and the residue triturated with boiling ether (2 × 50 mL). Additional ether was added so that the total volume was 180 mL. The crude ketone was then passed through a 10 × 2 cm column of Florisil (60/100 mesh, prepacked using dry ether) and the solvent removed. Short-path distillation afforded 1.40 g (74%) of **7c**: bp 75–80 °C (0.3–0.5 mm); NMR δ 1.34 (d, 3 H, J = 6 Hz), 3.93 (apparent quintet, H, J = 6 Hz), 4.69 (s, 2 H), 4.9–5.4 (2 H), 5.5–6.2 (m, H), 7.2–7.6 (3 H), 7.6–8.0 (m, 2 H); MS, m/e 190 (1), 175 (1), 120 (87), 105 (100), 91 (30), 77 (48), 55 (38).

2-(2-Methyl-3-butenyl) Phenacyl Ether [[(1,1-Dimethylallyl)oxy]acetophenone, 7d]. By a procedure analogous to that employed for synthesis of 2-[(1-methylallyl)oxy]-1-phenylethanol but without THF or HMPA vide supra, 2-methyl-3-buten-2-ol was reacted with 0.1 mol of styrene oxide to afford *2-[(1,1-dimethylallyl)oxy]-1-phenylethanol* in 30% yield: bp 105–120 °C (0.4–0.6 mm); NMR δ 1.28 (s, 6 H), 2.94 (br s, H), 3.1–3.7 (2 H), 4.76 (dd, H, J = 8, 4 Hz), 4.85–5.25 (2 H), 5.81 (dd, H, J = 18, 10 Hz), 7.28 (5 H); MS, m/e 206 (2), 191 (1), 137 (21), 108 (23), 107 (100), 79 (34), 77 (19), 70 (53), 69 (36).

As in the preparation of **7c**, to PCC (20 mmol) and CH_2Cl_2 (30 mL) was added the [(dimethylallyl)oxy]phenylethanol (2.06 g, 10 mmol). After the mixture was stirred for 12 h, workup afforded 1.90 g (93% yield) of a clear liquid (98% pure by NMR) and distillation afforded 1.70 g (83% yield) of **7d**: bp 85–95 °C (0.3–0.4 mm); NMR δ 1.33 (s, 6 H), 4.56 (s, 2 H), 4.9–5.4 (2 H), 5.88 (dd, H, J = 18, 10 Hz), 7.2–7.6 (3 H), 7.7–8.1 (m, 2 H); MS, m/e 204 (22), 189 (4), 119 (14), 106 (27), 105 (100), 91 (18), 77 (30), 69 (42).

2-(2-Cyclopentenyl) Phenacyl Ether [(2-Cyclopentenyloxy)acetophenone, 7f]. A procedure analogous to that employed for synthesis of 2-[(1-methylallyl)oxy]-1-phenylethanol, cyclopent-2-enyl alcohol and styrene oxide afforded *2-[(2-cyclopentenyloxy)-1-phenylethanol* in 34% yield: bp 115–125 °C (0.1–0.2 mm); NMR δ 1.6–2.6 (4 H), 2.97 (H), 3.17–3.76 (2 H), 4.5–4.7 (H), 4.82 (dd, H, J = 8.5, 4 Hz), 5.92 (m, 2 H), 7.30 (5 H). Oxidation of this allyloxy alcohol (2.04 g, 10 mmol) with PCC (20 mmol) for 12 h yielded 1.75 g (87%) of **7f**: bp 105–110 °C (0.25 mm); NMR δ 1.8–2.8 (4 H), 4.56–4.86 (3 H), 5.97 (m, 2 H), 7.2–7.6 (m, 3 H), 7.8–8.1 (m, 2 H).

3-Methyl-2-butenyl Acetonyl Ether [(Prenyloxy)acetone, 7g]. As in the synthesis of **3a** outlined above, propylene oxide (5.8 g, 0.10 mol), 3-methyl-2-buten-1-ol (20 mL, 17.0 g, 0.20 mol), and NaH (57%, 8.42 g, 0.20 mol) gave *1-[(3,3-dimethylallyl)oxy]-2-propanol* in 82% yield: bp 85–90 °C (5 mm); NMR δ 1.05 (d, 3 H, J = 6 Hz), 1.66, 1.74 (2 s, 6 H), 2.43 (s, H), 2.9–3.7 (3 H), 3.92 (complex d, 2 H), 5.25 (complex t, H, J = 6 Hz). Oxidation[14] of this hydroxy ether (1.44 g, 10 mmol) with 20 mmol of pyridinium chlorochromate in CH_2Cl_2 for 3 h provided 1.06 g (75%) of **7g** (oxidation by Jones reagent gave a much lower yield, ca. 50%): bp 65–67 °C (5 mm); NMR δ 1.69 (s, 3 H), 1.77 (s, 3 H),

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2.15 (s, 3 H), 3.9–4.2 (4 H), 5.35 (complex t, H, J = 6 Hz); MS, m/e 142 (1), 127 (2), 85 (100), 69 (89), 43 (29), 41 (56).

Allyl Acetonyl Ether [(Allyloxy)acetone, 7f]. Sodium cyanide (82 g, 1.67 mol) was slowly added to solution of aqueous formaldehyde (38%, 150 mL, 2.0 mol) in methanol (150 mL) in a 1-L flask. The solution was stirred magnetically until homogeneous (about 1 h) at which time allyl bromide (202 g, 1.67 mol) in methanol (200 mL) was added dropwise (1 drop/2–3 s). The mixture was then refluxed for 15–20 min and cooled, H_2O (500 mL) added to dissolve the salt generated, and the resultant mixture was extracted with ether–pentane (1:1, 5 × 200 mL). Solvent removal via rotary evaporation left a yellow liquid that was distilled to give 79 g (49%) of *(allyloxy)acetonitrile*: bp 67–69 °C (25 mm) [lit.[18b] bp 149–157 °C); NMR δ 3.70–4.30 (4 H), 5.0–5.6 (2 H), 5.6–6.3 (m, H).

To a flame-dried 500-mL three-necked flask were added magnesium turnings (14.6 g, 0.60 mol, oven dried) and dry ether (100 mL) followed by dropwise addition of a solution of methyl iodide (38 mL, 86.6 g, 0.61 mol) in dry ether (50 mL) with stirring under nitrogen. After refluxing for 2 h, the allyloxy nitrile (30 g, 0.309 mol) in dry ether (100 mL) was added dropwise with cooling over 15–20 min; two layers then appeared that were vigorously stirred overnight at room temperature. The residue was quenched by addition of H_2O (50 mL), acidified with 6 M H_2SO_4, and separated, and the aqueous layer was extracted with ether (4 × 50 mL). The combined ethereal extracts were washed with aqueous $NaHCO_3$ (2 × 20 mL) and aqueous saturated NaCl (2 × 50 mL) and dried (Na_2SO_4). Solvent removal and distillation of the residue gave 15.6 g (44%) of **7f**: bp 55–58 °C (15 mm); NMR δ 2.14 (s, 3 H), 3.95–4.15 (4 H), 5.05–5.50 (2 H), 5.6–6.2 (m, H). An analytical sample was obtained via preparative GLPC (column C, 180 °C).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.12; H, 8.85. Found: C, 62.93; H, 8.91.

3-Methyl-2-butenyl Acetonyl Ether [(Prenyloxy)acetone, 7g]. In like manner (vide supra), formaldehyde (2.0 mol), NaCN (1.1 mol), and 2-methyl-4-chloro-2-butene (prenyl chloride, 1.0 mol) gave 38 g (30%) of *(prenyloxy)acetonitrile*: bp 75–85 °C (9–10 min); NMR δ 1.76 (6 H), 3.82 (d, 2 H, J = 4 Hz), 4.20 (s, 2 H), 5.34 (complex t, H, J = 7 Hz); MS, m/e 124 (3), 110 (97), 85 (28), 83 (34), 69 (78), 68 (44), 57 (32), 55 (34), 43 (45), 41 (100), 39 (41). This nitrile reacted with methylmagnesium iodide as above to yield 12.6 g (55%) of **7g**, bp 65–70 °C (5 mm). This product showed ^{1}H NMR and mass spectra identical with those of the same compound prepared from propylene oxide and allyl alcohol (vide supra).

Synthesis of 2-Methoxyallyl Ethers. To a flame-dried, 250-mL Morton flask equipped with a condenser and mechanical stirrer was added NaH (57% in oil, 6.4 g, 170 mmol) that was washed with pentane (2 × 50 mL). THF (150 mL) and HMPA (15–20 mL) were added followed by dropwise addition (over 30 min) of 3-methyl-2-butenol (13 g, 150 mmol) to the hydride suspension. After the addition, the mixture was refluxed under nitrogen until hydrogen evolution ceased; 2-methoxyallyl bromide[15] (14 mL, 19.6 g of 65%, 84 mmol) was then added dropwise (over 15–20 min). The mixture was again refluxed for 1 h, cooled, poured into ice water (100 mL), and extracted with pentane (2 × 150 mL). The organic extracts were washed with H_2O (5 × 50 mL) and aqueous saturated NaCl (2 × 50 mL) and dried (Na_2SO_4). The solvent was removed via rotary evaporation, and the residue then distilled over a short-path condenser. The (allyloxy)methoxypropenes produced were at least 90–95% pure as determined by GLPC (columns A, D, or E, 120–180 °C). The usual impurity was the ketone formed by partial hydrolysis. The enol ether remains "NMR pure" in the absence of water and acid.

1-Cyclopentenylcarbinyl 2-Methoxyallyl Ether (11h). From 1-cyclopentenylcarbinol: bp 110–115 °C (10 mm); NMR δ 1.7–2.1 (2 H), 2.1–2.5 (4 H), 3.57 (s, 3 H), 3.87 (s, 2 H), 3.95–4.25 (4 H), 5.62 (br s, H); MS, m/e 168 (12), 139 (33), 97 (67), 88 (89), 81 (100), 79 (64), 73 (20), 72 (31), 67 (23), 69 (27), 43 (55), 41 (48).

Cyclohex-2-enyl 2-Methoxyallyl Ether (11i). From cyclohex-2-enol: bp 115–125 °C (10 mm); NMR δ 1.5–2.2 (6 H), 3.58 (s, 3 H), 3.8–4.3 (5 H), 5.83 (2 H); MS, m/e 168 (19), 153 (1), 139 (47), 107 (34), 88 (100), 81 (56), 79 (37), 73 (26), 72 (22), 59 (31).

1-Cyclohexenylcarbinyl 2-Methoxyallyl Ether (11j). From 1-cyclohexenylcarbinol: bp 126–136 °C (10 mm); NMR δ 1.4–1.8 (4 H), 1.8–2.3 (4 H), 3.69 (s, 3 H), 3.86 (4 H), 3.95–4.25 (2 H), 5.70 (br s, H); MS, m/e 182 (14), 167 (1), 153 (40), 111 (11), 95 (58), 88 (100), 79 (28), 72 (32), 67 (32), 41 (29).

1-Vinylcyclohexyl 2-Methoxyallyl Ether (11k). From 1-vinylcyclohexanol: bp 125–127 °C (10 mm); NMR δ 1.2–2.1 (10 H), 3.53 (s, 3 H), 3.70 (s, 2 H), 4.00 (d, H, J = 2 Hz), 4.21 (m, H), 4.9–5.3 (2 H), 5.78 (dd, H, J = 18, 9 Hz); MS, m/e 196 (4), 167 (49), 135 (39), 109 (39), 93 (24), 88 (100), 85 (25), 67 (45), 55 (23).

Cyclohept-2-enyl 2-Methoxyallyl Ether (11m). From cyclohept-2-enol: bp 125–127 °C (10 mm); NMR δ 1.3–2.3 (8 H), 3.55 (s, 3 H), 3.90 (s, 2 H), 3.98–4.30 (3 H), 5.79 (2 H); MS, m/e 182 (14), 153 (54), 121 (34), 111 (15), 95 (55), 93 (31), 88 (100), 79 (31), 73 (26), 67 (33), 59 (38).

Cyclooct-2-enyl 2-Methoxyallyl Ether (11n). From cyclooct-2-enol: bp 135–137 °C (10 mm); NMR δ 1.2–2.3 (10 H), 3.57 (s, 3 H), 3.85–4.50 (5 H), 5.3–6.0 (2 H); MS, m/e 196 (16), 16 (24), 125 (23), 109 (39), 88 (100), 72 (22), 67 (54), 55 (29), 43 (25), 41 (26).

Cinnamyl 2-Methoxyallyl Ether (11o). The 2-methoxyallylation of cinnamyl alcohol was carried out in the usual manner (vide supra), and the distilled product was immediately hydrolyzed to the corresponding allyloxy ketone (vide infra).

Hydrolysis of 2-Methoxyallyl Ethers. To the above enol ethers (6–10 g) in a 2–3-fold volume of ethyl ether–tetrahydrofuran solution (1:1) was added 1 N HCl (2–3 mL). The cloudy or two-phase mixture was vigorously stirred magnetically for 30–60 min and separated, and the organic layer was washed with aqueous $NaHCO_3$ (50% saturated, 2 × 10 mL). The combined aqueous layers were then reextracted with ether (3 × 10 mL). The organic layers were combined, washed with aqueous $NaHCO_3$ (5 mL), H_2O (5 mL), and aqueous saturated NaCl (3 × 10 mL), and dried (Na_2SO_4). Removal of the solvent, followed by distillation afforded the allyloxy ketones (allyl acetonyl ethers) in 80–97% yield (overall from alcohol, see Table I).

1-Cyclopentenylmethyl Acetonyl Ether [[(1-Cyclopentenylcarbinyl)oxy]acetone, 7h]: bp 106–8 °C (10 mm); NMR δ 1.5–2.6 (6 H), 2.14 (s, 3 H), 3.97 (s, 2 H), 4.10 (br s, 2 H), 5.66 (br s, H); MS, m/e 154 (4), 111 (8), 98 (18), 97 (100), 81 (85), 80 (40), 79 (44), 58 (31), 43 (46).

2-Cyclohexenyl Acetonyl Ether [(2-Cyclohexenyloxy)acetone, 7i]: bp 60–62 °C (1 mm); NMR δ 1.5–2.6 (6 H), 2.17 (s, 3 H), 3.7–4.2 (2 H), 4.06 (s, 2 H), 5.84 (m, 2 H); MS, m/e 145 (1), 139 (1), 111 (3), 98 (11), 97 (68), 81 (100), 80 (36), 79 (48), 43 (43).

1-Cyclohexenylmethyl Acetonyl Ether [[(1-Cyclohexenylcarbinyl)oxy]acetone, 7j]: bp 68–73 °C (1 mm); NMR δ 1.3–1.8 (4 H), 1.8–2.4 (4 H), 2.14 (3 H, s), 3.8–4.1 (4 H), 5.71 (bs, H); MS, m/e 168 (4), 153 (1), 112 (22), 111 (100), 95 (85), 94 (49), 81 (22), 67 (58), 55 (32), 43 (43).

1-Vinylcyclohexyl Acetonyl Ether (7k): bp 123–124 °C (10 mm); NMR δ 1.2–2.0 (10 H), 2.17 (s, 3 H), 3.80 (s, 2 H), 4.9–5.3 (2 H), 5.5–6.0 (H); MS, m/e 182 (5), 167 (1), 139 (6), 125 (16), 109 (100), 94 (39), 67 (71), 57 (15), 55 (32), 43 (32).

2-Cycloheptenyl Acetonyl Ether [(2-Cycloheptenyloxy)acetone, 7m]: bp 125–127 °C (10 mm); NMR δ 1.3–2.4 (8 H), 2.16 (s, 3 H), 3.9–4.2 (H), 4.02 (s, 2 H), 5.79 (m, 2 H); MS, m/e 168 (1), 125 (5), 111 (85), 95 (100), 79 (36), 67 (48), 43 (41).

2-Cyclooctenyl Acetonyl Ether [(2-Cyclooctenyloxy)acetone, 7n]: bp 136–138 °C (10 mm); NMR δ 1.2–1.8 (8 H), 1.9–2.4 (2 H), 2.15 (s, 3 H), 4.04 (s, 2 H),4.0–4.6 (H), 5.2–6.0 (2 H); MS, m/e 182 (4), 139 (18), 125 (100), 109 (69), 81 (49), 67 (86), 57 (40), 55 (53), 43 (51), 41 (36).

Cinnamyl Acetonyl Ether [(Cinnamyloxy)acetone, 7o]: bp 115–120 °C (1 mm); NMR δ 2.13 (s, 3 H), 4.06 (s, 2 H), 4.20 (d, 2 H, J = 5 Hz), 6.21 (dt, H, J = 16, 5 Hz), 6.65 (d, H, J = 16 Hz), 7.1–7.5 (5 H); MS, m/e 175 (38), 143 (44), 128 (14), 118 (15), 117 (100), 115 (22), 91 (11), 43 (12).

Claisen Rearrangement of Allyloxy Ketone Enol Silyl Ethers. Typical procedure: To a flame-dried 50-mL round-bottom flask, equipped with a condenser, magnetic stirring bar, and nitrogen blanket, was added via syringe DMF (10 mL), triethylamine (2.53 g, 3.5 mL, 25 mmol), and chlorotrimethylsilane (Me_3SiCl) (1.3 g, 1.6 mL, 12.5 mmol). After a few minutes, a precipitate of triethylamine hydrochloride appeared (due to the presence of small amounts of HCl formed by hydrolysis of Me_3SiCl) and a slight discoloration of the solution took place. It

was important that a good excess of the above reagents be used to ensure complete reaction of the allyloxy ketone. Failure to do so resulted in material that prematurely polymerized or decomposed. The appropriate allyloxy ketone (10.0 mmol) was then introduced via syringe and additional DMF (5 mL) added. The solution was refluxed (130–140 °C) for 16–20 h and cooled, and pentane (20 mL) was added. The light to dark brown two-phase slurry was transferred to a separatory funnel and the lower layer extracted with pentane (3 × 20 mL). The combined pentane extracts were washed with *cold* aqueous $NaHCO_3$ (50% saturated, 2 × 10 mL) and the washings added to the extracted reaction mixture. The now homogeneous solution was then reextracted with pentane (3 × 10 mL). All pentane extracts were combined and *quickly* washed with *cold* aqueous 1.5 M HCl (3 × 10 mL), *cold* aqueous $NaHCO_3$ (10 mL), H_2O (10 mL), and aqueous saturated NaCl (2 × 10 mL). The resulting pentane solution was dried (Na_2SO_4) and concentrated via rotary evaporation to afford a crude product in 90–99% yield. Vacuum distillation then gave an 80–99% yield of purified product.

2-Phenyl-2-(trimethylsiloxy)-4-pentenal (14a). From allyl phenacyl ether [(allyloxy)acetophenone, **7a**] in 85% yield: bp 70–73 °C (0.05 mm); NMR δ 0.19 (s, 9 H), 2.86 (complex d, 2 H, J = 7 Hz), 4.8–5.2 (2 H), 5.3–6.0 (H), 7.37 (5 H), 9.59 (s, H); MS, m/e 233 (16), 219 (100), 107 (15), 192 (28), 129 (21), 77 (7), 75 (16), 74 (15), 73 (74). An analytical sample was obtained via preparative GLPC (column B, 190 °C). Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.68; H, 8.31. Found: C, 67.70; H, 8.15.

3-Methyl-2-phenyl-2-(trimethylsiloxy)-4-pentenal (14b). From 2-butenyl phenacyl ether [(crotyloxy)acetophenone] in 98% yield: NMR analysis shows the presence of two different aldehydic protons and two different groups of methyl protons. It is, therefore, evident that a 60:40 mixture of diastereomers was formed: NMR δ 0.18 (s, 9 H), 0.82, 1.03 (2 d (60% and 40%, respectively), 3 H, J = 6.5 Hz), 2.98 (apparent pentet, H, J = 6.5 Hz), 4.8–5.3 (2 H), 5.3–6.2 (m, H), 7.38 (5 H), 9.78, 9.83 (2 s (60% and 40%, respectively), H); MS, m/e 262 (2), 247 (31), 233 (100), 208 (32), 107 (94), 192 (39), 157 (45), 143 (55), 77 (13), 75 (24), 73 (77), 55 (12).

2-Phenyl-2-(trimethylsiloxy)-4-hexenal (14c). From 2-(3-butenyl) phenacyl ether [[(1-methylallyl)oxy]acetophenone] in 85% yield: NMR δ 0.16 (s, 9 H), 1.57 (complex d, 3 H, J = 5 Hz), 2.65–2.85 (2 H), 5.2–5.5 (2 H), 7.32 (5 H), 9.53 (s, H); MS, m/e 262 (1), 247 (13), 234 (26), 233 (84), 208 (49), 192 (19), 143 (28), 77 (7), 72 (26), 73 (100), 45 (27).

5-Methyl-2-phenyl-2-(trimethylsiloxy)-4-hexenal (14d). From 2-(2-methyl-3-butenyl) phenacyl ether [[(1,1-dimethylallyl)oxy]acetophenone, **7d**] in 99% yield: NMR δ 0.15 (s, 9 H), 1.55 (br s, 3 H), 1.61 (br s, 3 H), 2.77 (br d, 2 H, J = 6.5 Hz), 5.02 (complex t, H, J = 6.5 Hz), 7.33 (5 H), 9.55 (s, H); MS, m/e 276 (5), 261 (14), 248 (21), 247 (64), 208 (36), 207 (62), 157 (35), 75 (28), 73 (100), 69 (30).

3,3-Dimethyl-2-phenyl-2-(trimethylsiloxy)-4-pentenal (14e). From 3-methyl-2-butenyl phenacyl ether [(prenyloxy)-acetophenone] in 99% yield: analysis by TLC showed essentially one major spot, but with a significant amount of tailing; NMR δ 0.08, 0.17 (2 s, 9 H), 0.98 (s, 3 H), 1.07 (s, 3 H), 4.8–5.2 (2 H), 5.99 (dd, H, J = 17, 11 Hz), 7.1–7.6 (5 H), 10.23 (s, H); MS, m/e 276 (7), 261 (18), 249 (13), 247 (100), 208 (63), 207 (100), 192 (33), 157 (58), 77 (9), 75 (24), 73 (86), 69 (36). An analytical sample was obtained of the major product by preparative GLPC. Anal. Calcd for $c_{16}H_{24}O_2Si$: C, 69.50; H, 8.77. Found: C, 69.77; H, 8.57.

2-(2-Cyclopentenyl)-2-phenyl-2-(trimethylsiloxy)acetaldehyde (14f). From 2-cyclopentenyl phenacyl ether [(2-cyclopentenyloxy)acetophenone] in 80% yield: NMR δ 0.14 (s, 9 H), 1.5–2.4 (4 H), 3.3–3.7 (H), 5.41 (m, H), 5.78 (m, H), 7.33 (5 H), 9.77 (s, H); MS, m/e 247 (1), 259 (4), 245 (30), 208 (60), 207 (31), 192 (29), 77 (5), 75 (16), 73 (100), 67 (24).

3,3-Dimethyl-2-methyl-2-(trimethylsiloxy)-4-pentenal (14g). From 3-methyl-2-butenyl acetonyl ether [(prenyloxy)-acetone] in 100% yield: bp 70–75 °C (4.5 mm); NMR δ 0.11 (s, 9 H), 1.01 (s, 6 H), 1.22 (s, 3 H), 4.7–5.2 (2 H), 5.7–6.3 (m, H), 9.62 (s, H); MS, m/e 214 (1), 199 (6), 186 (15), 185 (15), 185 (87), 146 (33), 145 (17), 84 (42), 75 (19), 73 (100), 69 (40). An analytical sample was secured (column C, 150 °C). Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.62; H, 10.36. Found: C, 61.48; H, 10.22.

2-(2-Methylenecyclopentyl)-2-(trimethylsiloxy)propanal (14h). From 1-cyclopentenylcarbinyl acetonyl ether in 91% yield: bp 52–53 °C (0.5 mm); NMR δ 0.14 (s, 9 H), 1.27, 1.33 (2 s, (55% and 45%, respectively), 3 H), 1.4–2.0 (4 H), 2.0–2.5 (2 H), 2.5–2.9 (H), 4.8–5.1 (2 H), 9.58 (s, H); MS, m/e 226 (3), 211 (16), 198 (33), 197 (100), 183 (23), 146 (23), 145 (42), 107 (26), 84 (19), 81 (19), 75 (28), 73 (82).

2-(2-Cyclohexenyl)-2-(trimethylsiloxy)propanal (14i). From 2-cyclohexenyl acetonyl ether [(2-cyclohexenyloxy)acetone] in 95% yield: bp 67–70 °C (0.6 mm); NMR δ 0.14 (s, 9 H), 1.27 (s, 3 H), 1.3–2.2 (6 H), 2.2–2.6 (H), 5.73 (br s, 2 H), 9.48 (s, H); MS, m/e 226 (3), 211 (16), 197 (100), 183 (18), 146 (66), 145 (36), 130 (36), 107 (44), 81 (44), 79 (21), 75 (25), 73 (92).

2-(2-Methylenecyclohexyl)-2-(trimethylsiloxy)propanal (14j). From 1-cyclohexenylcarbinyl acetonyl ether were obtained two major products in 95% yield. NMR analysis shows a 1:1 mixture of diastereomers: bp 70–75 °C (0.5 mm); NMR δ 0.14 (s, 9 H), 1.28, 1.32 (2 s, (50% and 50%, respectively), 3 H), 1.4–2.5 (9 H), 4.63 (br s, H), 4.73, 4.85 (2 br s, H), 9.58 (s, H); MS, m/e 240 (7), 225 (16), 212 (31), 211 (100), 146 (34), 145 (25), 130 (20), 121 (30), 95 (18), 75 (23), 73 (68).

4-Cyclohexylidene-2-methyl-2-(trimethylsiloxy)butanal (14k). From 1-vinylcyclohexyl acetonyl ether in 95% yield: bp 81–84 °C (0.5 mm); NMR δ 0.13 (s, 9 H), 1.25 (s, 3 H), 1.4–1.8 (6 H), 1.9–2.5 (6 H), 5.07 (t, H, J = 8 Hz), 9.47 (s, H); MS, m/e 245 (6), 239 (10), 226 (19), 225 (52), 147 (26), 146 (100), 135 (41), 130 (46), 109 (37), 75 (20), 73 (57), 67 (37).

2-(2-Cycloheptenyl)-2-(trimethylsiloxy)propanal (14m). From 2-cycloheptenyl acetonyl ether [(2-cycloheptenyloxy)-acetone] in 95% yield: bp 72–74 °C (0.5 mm); NMR δ 0.14 (s, 9 H), 1.27 (s, 3 H), 1.0–2.3 (8 H), 2.3–2.7 (H), 5.4–6.0 (2 H), 9.47 (s, H); MS, m/e 240 (1), 225 (10), 212 (35), 211 (100), 146 (55), 145 (15), 130 (25), 121 (44), 117 (25), 95 (43), 93 (30), 75 (27), 73 (75).

2-(2-Cyclooctenyl)-2-(trimethylsiloxy)propanal (14n). From 2-cyclooctenyl acetonyl ether [(2-cyclooctenyloxy)acetone] in 95% yield: bp 83–85 °C (0.5 mm); NMR (diastereomers) δ 0.15, 0.17 (2 s (65% and 35%, respectively), 9 H), 1.0–2.3 (13 H), 2.3–2.9 (H), 5.3–6.0 (2 H), 9.53, 9.57 (2 s (35% and 65%, respectively), H); MS, m/e 254 (2), 239 (6), 226 (26), 225 (100), 146 (24), 145 (5), 130 (15), 117 (21), 109 (20), 75 (16), 73 (58), 67 (29).

2-Methyl-3-phenyl-2-(trimethylsiloxy)-4-pentenal (14o). From cinnamyl acetonyl ether [(cinnamyloxy)acetone, **7o**] in 89% yield: the Claisen product is clearly a 7:3 mixture of diastereomers since two different aldehydic and methyl proton absorptions are present; bp 80–95 °C (0.3–0.4 mm); NMR δ 0.10 (s, 9 H), 1.10, 1.32 (2 s (70% and 30%, respectively), 3 H), 4.8–5.3 (2 H), 5.9–6.6 (H), 7.27 (5 H), 9.37, 9.62 (2 s, H); MS, m/e 262 (4), 247 (3), 234 (21), 233 (70), 146 (14), 145 (75), 143 (36), 118 (20), 117 (97), 115 (25), 75 (21), 73 (100).

2-Methyl-2-(trimethylsiloxy)-4-pentenal (14p). From allyl acetonyl ether [(allyloxy)acetone, **7p**] in 70% yield: bp 64–66 °C (15 mm); NMR δ 0.15 (s, 9 H), 1.28 (s, 3 H), 2.36 (d, 2 H, J = 7 Hz), 4.8–5.3 (2 H), 5.4–6.2 (m, H), 9.53 (s, H); MS, m/e 17 (27), 157 (100), 145 (31), 130 (25), 127 (27), 75 (25), 73 (89), 41 (7), 29 (2). an analytical sample was obtained via preparative GLPC (column C, 150 °C). Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74. Found: C, 57.85; H, 9.76.

Synthesis of Allyl Ketones by Hydrolysis and Oxidation of α-Aryl (and Alkyl)-α-(trimethylsiloxy) γ,δ-Unsaturated Aldehydes. Oxidation of the α-trimethylsiloxy aldehydes by any of the three procedures described below provided β,γ-unsaturated ketones (allyl ketones). Prehydrolysis of the silyl ethers was carried out in the following typical manner: To a 10-mL round-bottom flask was added a magnetic stirring bar, methanol (5 mL), H_2O (1 mL), a catalytic amount (1–3 mg) of *p*-toluenesulfonic acid, and the siloxy aldehyde (300 μL, about 1 mmol). Two phases were initially present, but after boiling under reflux (about 1 h), one phase was usually found. The hydrolyzed material could then be isolated via rotary evaporation of solvents or oxidized in situ.

Method 1: Jones Oxidation.[24] For these oxidations, pre-

(24) (a) Krumpole, M.; Rocek, J. *J. Am. Chem. Soc.* **1976**, *98*, 872; **1977**, *99*, 137. (b) Djerassi, C.; Engle, R. R.; Bowers, A. *J. Org. Chem.* **1956**, *21*, 1547.

hydrolysis was not carried out since the 6–30-h-reaction period employed usually completely hydrolyzed all of the α-siloxy aldehydes investigated. Typically, to an ice-chilled solution of the α-siloxy aldehyde (300 μL, 1.0–1.3 mmol) in acetone (5 mL) was added dropwise (1 drop/2–3 s) a snall excess (1 mol equiv) of Jones reagent (1.75 M). The ice bath was removed and the reaction allowed to reach room temperature. Reaction progress was followed by TLC until usually only one major spot (ketone) was observed. The mixture was then cooled, diluted with H_2O (15 mL) and extracted with pentane (5 × 10 mL). The pentane extracts were washed with aqueous $NaHCO_3$ (50% saturated, 2 × 10 mL), H_2O (10 mL), and aqueous saturated NaCl (2 × 10 mL) and dried (Na_2SO_4). Solvent removal by rotary evaporation provided the β,γ-unsaturated ketone.

Method 2. Periodic Acid Oxidation.[25] For these oxidations, all compounds (300 μL, 1.0–1.3 mmol) were prehydrolyzed as described (vide supra) and then oxidized in situ by a 10–20% molar excess of a standard solution of periodic acid ($HIO_4 \cdot 2H_2O$, 1.002 M) at room temperature (1–10 h). Reaction progress was monitored via TLC and finally quenched by addition of ethylene glycol (50 μL, 0.90 mmol) followed by workup as previously described for method 1. The most severe problem in using this method of oxidation was the apparent decomposition of the product or inorganic iodine-containing products during solvent removal. Occasionally, the clear pentane extract would also turn pink while drying over Na_2SO_4. The extent to which this occurred was time dependent—the more quickly the product was dried and the solvent removed, the less this seemed to be a problem. For some oxidations, however, nothing seemed to inhibit this process—even copious washing with aqueous Na_2SO_3 (sodium sulfite) and/or $Na_2S_2O_3$ (sodium thiosulfate) failed to prevent the pink color's appearance. The pentane extract, which had turned pink when worked up as described, was usually found to have been *partially* isomerized to the more stable β,γ-unsaturated ketones as determined by NMR. It was later observed that a low-intensity light level during workup and darkness during drying *eliminated, or at least attenuated*, this type of decomposition. For these substrates, either Jones oxidation (CrO_3, aqueous H_2SO_4) or the less acidic sodium periodate oxidation ($NaIO_4$, aqueous HOAc) was usually satisfactory, albeit giving a lower yield.

Method 3. Sodium Periodate Oxidation.[26] $NaIO_4$ (428 mg, 2.0 mmol) was added to a 10-mL round-bottom flask containing acetone (4 mL), glacial acetic acid (2 mL), H_2O (1 mL), and a magnetic stirring bar. After thorough dissolution (ca. 1 h), the appropriate α-siloxy aldehyde (300 μL, 1.0–1.3 mmol) was added. Within a few minutes, a flocculent precipitate appeared and the resulting slurry was vigorously stirred for 2–6 h *under subdued lighting*. Reaction progress was monitored via TLC. After completion, the mixture was quenched with ethylene glycol (100 L, 1.8 mmol). Pentane extraction, workup, and solvent removal usually provided one major product. For some substrates, hydrolysis was slow and an extended reaction period or a higher temperature was needed. Also, quantitative recovery of the unreacted siloxy aldehyde and ketone product was generally achieved after workup and solvent removal. Thus, decomposition seemed to be less of a problem with this method than with the periodic acid oxidation.

1-Phenyl-3-buten-1-one (4a)[10,11c,19f] was prepared by oxidation of 2-phenyl-2-(trimethylsiloxy)-4-pentenal. An internal standard was used to determine and optimize the various reaction parameters with this substrate (see Table II). Thus, a standard solution of this siloxy aldehyde (distilled, 1.10 g, 4.42 mmol) and cyclododecane (57.3 mg, 0.340 mmol) was prepared and the "zero time" reaction ratio determined via NMR integration: area (δ 2.85, allylic protons)/area (δ 1.35, cyclododecane) = 0.70. Since there is no overlap of the starting material allylic protons (at δ 2.85) and the product allylic protons (at δ 5.0–5.4), the absolute yield was determined from the ratio of their respective peak integrations. Preparative reactions were carried out without an internal standard, and these yields are based on the weight of isolated product and its purity as determined as via GLPC (column B, 190 °C) and TLC. The title compound showed the following: NMR[19f] δ 3.73 (complex d, H, J = 6.5 Hz), 5.0–5.4 (2 H), 5.7–6.5 (m, H), 7.2–7.6 (3 H), 7.8–8.1 (2 H); MS, m/e 146 (39), 145 (22), 105 (100), 77 (48), 51 (18), 41 (6). An analytical sample was obtained via GLPC (column B, 180 °C). Anal. Calcd for $C_{10}H_{10}O$: C, 82.15; H, 6.90. Found: C, 82.07; H, 7.07.

TLC analysis of the hydrolyzed α-siloxy aldehyde showed only one product (R_f 0.37) different from the siloxy aldehyde (R_f 0.58); the NMR spectrum showed little change except for the absence of the peak at δ 0.09 ($-OSi(CH_3)_3$).

2-Methyl-1-phenyl-3-buten-1-one (4b). Oxidation of the prehydrolyzed siloxy aldehyde **14b** (300 μL, 1.15 mmol) by method 2 (1.30 mmol HIO_4) for 40 min gave an 83% yield of the ketone, which exhibited only one peak (ca. 95% purity) via GLPC (column B, 190 °C; or column D, 170 °C) and TLC: NMR δ 1.33 (d, 3 H, J = 6.5 Hz), 4.17 (apparent pentet, H, J = 6.5 Hz), 4.9–5.4 (2 H), 5.7–6.4 (m, H), 7.2–7.7 (3 H), 7.8–8.1 (2 H); MS, m/e 160 (4), 145 (2), 106 (14), 105 (100), 77 (71), 55 (6), 51 (30). An analytical sample was obtained via GLPC (column A, 170 °C). Anal. Calcd for $C_{11}H_{12}O$: C, 82.56; H, 7.57. Found: C, 82.31; H, 7.80.

1-Phenyl-3-penten-1-one (4c).[10e,i] Oxidation of the prehydrolyzed siloxy aldehyde **14c** (300 μL, 1.18 mmol) by method 2 (1.30 mmol HIO_4) for 2 h afforded the ketone in 83% yield. Analysis by GLPC (column D, 170 °C), NMR, and TLC showed a purity of ca. 95%: NMR δ 1.6–1.8 (m, 3 H), 3.5–3.8 (2 H), 5.5–5.8 (2 H), 7.1–7.6 (3 H), 7.8–8.1 (2 H); MS, m/e 160 (4), 106 (8), 105 (100), 51 (38). An analytical sample was obtained via GLPC (column B, 170 °C). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.57. Found: C, 82.46; H, 7.74.

4-Methyl-1-phenyl-3-penten-1-one (4d).[21] After prehydrolysis of **14d** (300 μL, 1.09 mmol), oxidation by method 2 for 2 h gave one product in 81% yield that was shown by TLC and GLPC (column D, 170 °C) to be at least 95% pure: NMR δ 1.70 (d, 3 H, J = 1.0 Hz), 1.75 (d, 3 H, J = 1.5 Hz), 3.67 (complex d, 2 H, J = 7 Hz), 5.41 (complex t, H, J = 7 Hz), 7.2–7.6 (3 H), 7.8–8.1 (2 H); MS, m/e 174 (14), 105 (16), 105 (100), 77 (75), 69 (7), 51 (28), 41 (34). An analytical sample was obtained via GLPC (column B, 180 °C). Anal. Calcd for $C_{12}H_{14}O$: C, 82.71; H, 8.11. Found: C, 82.42; H, 8.22.

2,2-Dimethyl-1-phenyl-3-buten-1-one (4e).[10j] Oxidation of the siloxy aldehyde **14e** (300 μL, 1.12 mmol) for 36 h by method 1 (3 equiv of Jones reagent) gave a 60% isolated yield of this ketone via preparative TLC. Jones oxidation led to one major product (ketone) but also a number of other unidentified products as determined via TLC and GLPC (column A, 170 °C). Oxidation of the prehydrolyzed **14e** by method 2 (1.25 mmol) for 40 min gave a 83% yield of ketone **4e**: NMR δ 1.38 (s, 6 H), 5.0–5.4 (2 H), 6.21 (dd, H, J = 17, 10 Hz), 7.2–7.5 (3 H), 7.7–8.0 (2 H); MS, m/e 174 (3), 106 (17), 105 (100), 77 (63), 69 (9), 51 (25), 41 (28). An analytical sample was obtained via GLPC (column A, 175 °C). Anal. Calcd for $C_{12}H_{14}O$: C, 82.70; H, 8.11. Found: C, 82.91; H, 8.39.

2-Cyclopentenyl Phenyl Ketone (4f).[10d] Oxidation of **14f** (300 μL, 1.09 mmol) by method 2 (1.35 mmol HIO_4) for 1 h afforded one product in 93% yield. Analysis by TLC and GLPC (column D, 170 °C) indicated only one product of ca. 98% purity: NMR δ 2.0–2.7 (4 H), 4.3–4.7 (H), 5.60–6.02 (2 H), 7.3–7.6 (3 H), 7.8–8.1 (2 H); MS, m/e 172 (11), 106 (13), 105 (100), 77 (75), 67 (22), 66 (11), 65 (22), 51 (29), 41 (28). An analytical sample was obtained via GLPC (column A, 170 °C). Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.04. Found: C, 83.73; H, 6.87.

3,3-Dimethyl-4-penten-2-one (4g).[4d,e,10f,h,17,20] Oxidation of **14g** (300 μL, 1.30 mmol) by method 1 (1.3 mmol of Jones reagent) gave a 68% yield of the ketone after a 20-h-reaction period. Analysis by TLC showed several products; analysis by GLPC (column B, 105 °C) showed two products (relative retention times 1.00/1.56) in a ratio of 95:5—the first of which was identified as the ketone **4g** and the second as unoxidized siloxy aldehyde **14g**. Method 2 (1.50 mmol of HIO_4) afforded an 80% yield of the crude ketone after a 36-h-reaction period (no prehydrolysis). Purity was ca. 90% via GLPC (column B, 150 °C, TC; column E, 120 °C, FID); NMR δ 1.21 (s, 6 H), 2.10 (s, 3 H), 4.9–5.3 (2 H), 5.96 (dd, H, J = 18, 10 Hz); reported[10f] NMR ($CDCl_3$) δ 1.18 (6 H, s), 2.05 (3 H, s), 5.0–5.3 (2 H, m), 5.8–6.3 (H, m); MS, m/e 112 (25), 97 (27), 70 (21), 69 (72), 59 (13), 43 (100), 41 (77). An analytical sample was obtained via GLPC (column B, 150 °C). Anal. Calcd

(25) (a) Prins, D. A.; Reichstein, T. *Helv. Chim. Acta* **1941**, *24*, 396, 945. (b) Reichstein, T.; Meystre, C.; Von Euw, J. *Ibid.* **1939**, *22*, 1107. (c) Schaffner, K.; Jeger, O. *Ibid.* **1962**, *45*, 400.

(26) Yanuka, Y.; Katz, R.; Sarel, S. *Tetrahedron Lett.* **1968**, 1725.

for $C_7H_{12}O$: C, 74.93; H, 10.80. Found: C, 74.97; H, 10.98.

2-Methylenecyclopentyl Methyl Ketone (4h). Oxidation of prehydrolyzed **14h** (300 μL, 1.29 mmol) by method 2 (1.42 mmol of HIO_4) for 2 h gave a pentane extract that turned pink during drying. Rewashing with aqueous $Na_2S_2O_3$ and redrying left a clear, yellow-tinted liquid in 63% yield after solvent removal. Analysis by GLPC (column B, 160 °C, TC; column E, 110 °C, FID) showed only one product that underwent partial (ca. 20%) thermal isomerization to the α,β-unsaturated ketone on passage through the column (relative retention time 1.50). The degree to which this isomerization occurred was dependent on the size of the sample injected (GC injection port temperature ca. 200 °C). The title compound showed the following: NMR δ 1.5–2.5 (6 H), 2.18 (s, 3 H), 3.2–3.6 (H), 4.94 (apparent q, H, J = 2 Hz), 5.06 (apparent q, H, J = 2 Hz); MS, m/e 124 (26), 109 (10), 86 (35), 84 (60), 81 (71), 80 (29), 43 (100). An analytical sample was obtained via GLPC (column B, 150 °C). Anal. Calcd for $C_8H_{12}O$: C, 77.36; H, 9.76. Found: C, 77.30; H, 9.58.

2-Cyclohexenyl Methyl Ketone (4i).[1a,5d,i,11b] A 2-h oxidation of prehydrolyzed **14i** (300 μL, 1.31 mmol) afforded a 72% yield of a single product: NMR δ 1.4–2.3 (6 H), 2.15 (s, 3 H), 2.9–3.3 (br s, H), 5.81 (br s, 2 H); reported[1a] NMR (CCl_4) δ 1.6–2.1 (6 H), 2.1 (s, 3 H), 3.0 (H), 5.8 (s, 2 H); MS, m/e 124 (70), 109 (3), 86 (27), 84 (38), 81 (100), 80 (47), 79 (45), 53 (27), 43 (88).

2-Methylenecyclohexyl Methyl Ketone (4j). Oxidation of prehydrolyzed **14j** (300 μL, 1.22 mmol) by method 2 for 2 h gave a 91% yield of a single major product via TLC and GLPC (column B, 180 °C): NMR δ 1.4–1.8 (6 H), 1.9–2.3 (2 H), 2.16 (s, 3 H), 3.0–3.3 (br s, H), 4.70 (bs, H), 4.88 (bs, H); MS, m/e 138 (38), 123 (13), 96 (29), 95 (100), 94 (33), 86 (73), 84 (92), 67 (35), 55 (20), 43 (82). An analytical sample was obtained via GLPC (column B, 150 °C). Anal. Calcd for $C_9H_{14}O$: C, 78.19; H, 10.23. Found: C, 77.89, H, 10.22.

4-Cyclohexylidene-2-butanone (4k).[22g] Oxidation of **14k** (300 μL, 1.15 mmol) by method 3 (2 mmol of $NaIO_4$) for 3 h and the use of subdued lighting conditions during the reaction and workup provided a 90% yield of a clear, yellow-tinted liquid containing ca. 85–90% of the ketone **4k** and a small amount of the residual, unrearranged acetonyl ether **7k**. The title ketone **4k** showed the following: NMR δ 1.3–1.8 (6 H), 1.9–2.3 (4 H), 2.13 (s, 3 H), 3.12 (d, 2 H, J = 7.5 Hz), 5.24 (complex t, H, J = 7.5 Hz); reported[22g] NMR (CCl_4) δ 1.50 (6 H), 2.03 (s, 3 H), 2.10 (m, 4 H), 3.05 (d, 2 H, J = 7.0 Hz); MS, m/e 152 (47), 137 (4), 109 (88), 94 (84), 81 (28), 79 (29), 67 (100), 55 (37), 43 (61), 41 (32).

2-Cycloheptenyl Methyl Ketone (4m). Oxidation of prehydrolyzed **14m** (300 μL, 1.24 mmol) by method 2 for 2 h gave an 84% yield of a single product: NMR δ 1.2–2.4 (8 H), 2.16 (s, 3 H), 3.1–3.5 (H), 5.6–6.1 (2 H); MS, m/e 138 (41), 123 (4), 95 (100), 94 (20), 86 (18), 84 (29), 67 (38), 43 (67). An analytical sample was obtained via GLPC (column B, 170 °C). Anal. Calcd for $C_9H_{14}O$: C, 78.19; H, 10.23. Found: C, 78.15; H, 10.41.

2-Cyclooctenyl Methyl Ketone (4n).[2f] Oxidation of prehydrolyzed **14n** (300 μL, 1.16 mmol) by method 2 (1.30 mmol of HIO_4) for 2 h afforded a 98% yield of a single major product. TLC showed the presence of a trace of residual acetonyl ether **7n**. The title ketone **4n** showed the following: NMR δ 1.3–2.6 (10 H), 2.15 (s, 3 H), 3.2–3.8 (H), 5.3–6.0 (2 H); MS, m/e 152 (45), 137 (6), 134 (14), 109 (68), 95 (40), 84 (12), 81 (28), 67 (100), 55 (37), 43 (100). An analytical sample was obtained via GLPC (column B, 180 °C). Anal. Calcd for $C_{10}C_{16}O$: C, 78.88; H, 10.61. Found: C, 79.04, H, 10.63.

3-Phenyl-4-penten-2-one (4o). Oxidation of the prehydrolyzed **14o** (300 μL, 1.20 mmol) by method 2 (1.30 mmol of HIO_4) for 2 h afforded two products in a ratio of 90:10 in a 94% yield. Analysis by NMR and GC/MS (column D, 150 °C) identified these as the title ketone **4o** and the residual, unrearranged acetonyl ether **7o** present in **14o**. Surprisingly, no rearrangement occurred during GLPC purification of **4o** (GC injection port temperatures less than 210 °C): NMR δ 2.12 (s, 3 H), 4.37 (d, H, J = 7.5 Hz), 4.8–5.4 (2 H), 5.9–6.6 (m, H), 7.29 (5 H); MS, m/e 160 (45), 145 (2), 118 (28), 117 (100), 115 (47), 91 (21), 86 (13), 84 (17), 43 (56). An analytical sample was obtained via GLPC (column A, 200 °C). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.57. Found: C, 82.61; H, 7.71.

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Registry No. **4a**, 6249-80-5; **4b**, 50599-02-5; **4c**, 73481-93-3; **4d**, 36597-09-8; **4e**, 62894-04-6; **4f**, 64207-12-1; **4g**, 4181-07-1; **4h**, 54683-73-7; **4i**, 29372-98-3; **4j**, 65756-02-7; **4k**, 21527-61-7; **4m**, 16554-78-2; **4n**, 31367-54-1; **4o**, 100702-66-7; **7a**, 65755-81-9; **7b**, 65755-84-2; **7c**, 100702-30-5; **7d**, 65755-83-1; **7e**, 65755-82-0; **7f**, 65755-85-3; **7g**, 54605-38-8; **7h**, 65755-89-7; **7i**, 65755-86-4; **7j**, 65755-90-0; **7k**, 100702-31-6; **7m**, 65755-87-5; **7n**, 65755-88-6; **7o**, 100702-32-7; **11h**, 100702-23-6; **11i**, 100702-24-7; **11j**, 100702-25-8; **11k**, 100702-26-9; **11m**, 100702-27-0; **11n**, 100702-28-1; **11o**, 100702-29-2; **14a**, 65755-91-1; **14b** (isomer 1), 100702-33-8; **14b** (isomer 2), 100702-34-9; **14c**, 100702-35-0; **14d**, 65755-94-4; **14e**, 65755-93-3; **14f**, 65755-96-6; **14g**, 65755-92-2; **14h** (isomer 1), 100702-36-1; **14h** (isomer 2), 100702-37-2; **14i**, 65755-97-7; **14j** (isomer 1), 100702-38-3; **14j** (isomer 2), 100702-39-4; **14k**, 100702-40-7; **14m**, 65755-98-8; **14n** (isomer 1), 100702-41-8; **14n** (isomer 2), 100702-42-9; **14o** (isomer 1), 100702-43-0; **14o** (isomer 2), 100702-44-1; **14p**, 100702-45-2; CH_2=$CHCH_2C(OH)PhCHO$, 100702-46-3; CH_2=$CHCH(CH_3)C(OH)PhCHO$ (isomer 1), 100702-47-4; CH_2=$CHCH(CH_3)C(OH)PhCHO$ (isomer 2), 100702-48-5; CH_3CH=$CHCH_2C(OH)PhCHO$, 100702-49-6; $(CH_3)_2C$=$CHCH_2C(OH)PhCHO$, 100702-50-9; CH_2=$CHC(CH_3)_2C(OH)PhCHO$, 100702-51-0; CH_2=$CHC(CH_3)_2C(OH)CH_3CHO$, 100702-53-2; CH_2=$CHCH(Ph)C(OH)CH_3CHO$ (isomer 1), 100702-63-4; CH_2=$CHCH(Ph)C(OH)CH_3CHO$ (isomer 2), 100702-64-5; CH_2=$CHCH_2C(OH)CH_3CHO$, 100702-65-6; CH_3CH=$CHCH_2OH$, 6117-91-5; $(CH_3)_2CH$=$CHCH_2OH$, 556-82-1; 2-[(1-methylallyl)oxy]-1-phenylethanol, 100702-19-0; 2-[(1,1-dimethylallyl)oxy]-1-phenylethanol, 100702-20-3; 2-[(2-cyclopentenyl)oxy]-1-phenylethanol, 100702-21-4; 1-[(3,3-dimethylallyl)oxy]-2-propanol, 54605-37-7; (prenyloxy)acetonitrile, 100702-22-5; (allyloxy)acetone, 53135-67-4; 2-(cyclopent-2-enyl)-2-phenyl-2-hydroxyacetaldehyde, 100702-52-1; 2-(2-methylenecyclopentyl)-2-hydroxypropanal (isomer 1), 100702-54-3; 2-(2-methylenecyclopentyl)-2-hydroxypropanal (isomer 2), 100702-55-4; 2-(2-cyclohexenyl)-2-hydroxypropanal, 100702-56-5; 2-(2-methylenecyclohexyl)-2-hydroxypropanal (isomer 1), 100702-57-6; 2-(2-methylenecyclohexyl)-2-hydroxypropanal (isomer 2), 100702-58-7; 4-cyclohexylidene-2-methyl-2-hydroxybutanal, 100702-59-8; 2-(2-cyclopentyl)-2-hydroxypropanal, 100702-60-1; 2-(2-cyclooctenyl)-2-hydroxypropanal (isomer 1), 100702-61-2; 2-(2-cyclooctenyl)-2-hydroxypropanal (isomer 2), 100702-62-3; diazoacetophenone, 3282-32-4; allyl alcohol, 107-18-6; 3-buten-2-ol, 598-32-3; styrene oxide, 96-09-3; 2-methyl-3-buten-2-ol, 115-18-4; 2-cyclopenten-1-ol, 3212-60-0; propylene oxide, 75-56-9; allyl bromide, 106-95-6; 2-methyl-4-chloro-2-butene, 503-60-6; 2-methoxypropene, 116-11-0; 2-methoxyallyl bromide, 26562-24-3; 1-cyclopentenylcarbinol, 1120-80-5; cyclohex-2-enol, 822-67-3; 1-cyclohexenylcarbinol, 4845-04-9; 1-vinylcyclohexanol, 1940-19-8; cyclohept-2-enol, 4096-38-2; cyclooct-2-enol, 3212-75-7; cinnamyl alcohol, 104-54-1; (allyloxy)acetonitrile, 51336-63-1.