Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 237B instrument. NMR spectra were obtained on a Hitachi Perkin-Elmer Model R-24.

Starting Materials. Phenylpropiolonitrile, bp 105–106 °C (13 mm), mp 35–36 °C (MeOH) (lit.[8] mp 41 °C), was best prepared from phenylpropiolic acid (Aldrich) via the acid chloride, bp 115–116 °C (17 mm), and amide, mp 108–109 °C. Numerous other attempts at synthesizing 1 and a series of phenyl-substituted analogues gave consistenly discouraging results.[8-10] Cinnamonitrile was purchased (Aldrich). α-Phenylcinnamonitrile was available.[3] The $NaBH_4$ (J. T. Baker) was used as received.

General Procedure. To 2.60 (0.020 mol) of cinnamonitrile in a 50-mL volumetric flask was added absolute EtOH. In another 50-mL volumetric flask 3.895 g (0.101 mol) of $NaBH_4$ was dissolved in absolute EtOH. These reactant solutions were equilibrated at the desired temperature (0 or 25 °C) and poured into a 250-mL round-bottom flask at the same temperature with mechanical stirring. At intervals, 10-mL aliquots were removed and quenched in 50 g of ice–water. Then 5% HCl was added dropwise until H_2 evolution ceased and the pH was about 2. Each aliquot was extracted with CCl_4 or $CHCl_3$ (4 × 5 mL). The combined organic extracts were washed with deionized water (3 × 25 mL). After drying overnight ($MgSO_4$), filtering, concentration to ca. 5 mL, and quantitative transfer to a 10-mL volumetric flask, the IR was recorded. The remaining content of the volumetric flask was transferred to a 20-cm test tube, and the volume was reduced to 1 mL. The NMR spectrum was then recorded.

Infrared Analyses. Matched cells of 0.2-mm path length were used. Beer's law was followed at the concentrations employed. The decreasing absorbance at 2280 cm^{-1} (1, CN) with time gave excellent data, which by appropriate treatment provided the half-life for propiolonitrile (1). The other triple bond peaks at 2145 and 2210 cm^{-1} interfered with tracking the formation of 2 (2220 cm^{-1}). The 2220-cm^{-1} (CN) peak was the marker for obtaining $t_{1/2}$ for independent reductions of cinnamonitrile (2) and α-phenylcinnamonitrile (3).

NMR Analyses. The aromatic protons of 1 are at δ 7.18–7.87. Cinnamonitrile (2) has its protons at ca. δ 7.34 (Ar), 5.78 (α-H, d), and 7.27 (β-H, d). The β-phenylpropionitrile (3) has aromatic protons at ca. δ 7.23 and methylene protons (m) between δ 3.02 and 2.32. Appropriate relative integrations allowed the determination of $t_{1/2}$ for individual compounds or of concentrations of different species for complex mixtures.

Registry No. 1, 935-02-4; 2, 4360-47-8; 4, 2510-95-4; $NaBH_4$, 16940-66-2.

---

(8) Cariou, M. *Bull. Soc. Chim. Fr.* **1969**, 215.
(9) Compagnon, P. L.; Grosjean, B. *Synthesis* **1976**, *7*, 448.
(10) Anton, D. R.; Crabtree, R. H. *Tetrahedron Lett.* **1983**, *24*, 2449.

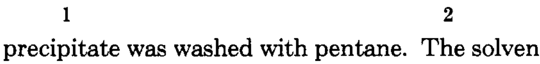
Communications

General Method for the Synthesis of Enol Ethers (Vinyl Ethers) from Acetals

Summary: A general, high yield method for the synthesis of enol ethers from acetals has been devised that involves treatment of an appropriate acetal with a 10–75% molar excess of trimethylsilyl triflate and a 20–90% molar excess of *N,N*-diisopropylethylamine at −20 to 25 °C. Yields ranged from 89 to 98%.

Sir: As part of a general study of the photoinduced single electron transfer promoted ring opening of alkoxy-substituted cyclopropanes,[1] access to a variety of enol ethers (vinyl ethers) was required. Simple alkylation of enolate anions generally yields C-alkylation rather than O-alkylation. Thus, the most frequently used method of enol ether synthesis has been the acid-catalyzed thermolysis of acetals[2] to eliminate an alcohol and produce the desired enol ether. More recently, several new methods of accomplishing this transformation have appeared.[3,4] However, many of these new procedures are either limited to narrow classes of compounds[4] or require reagents that are neither attractive to organic chemists nor readily available in organic chemistry laboratories.[3b] Consideration of the mechanistic details of the use of trimethylsilyl triflate as a catalyst for the formation of acetals[5] led us to explore the use of trimethylsilyl triflate as a stoichiometric reagent for the conversion of acetals into enol ethers. We now report that a wide variety of acetals are converted into the corresponding enol ethers in 89–98% yields on reaction with 1.10–1.75 equiv of trimethylsilyl triflate and 1.20–1.90 equiv of *N,N*-diisopropylethylamine at −20 to 25 °C in dichloromethane.

In a general procedure for dimethyl acetals, 1, 1.0 equiv of the dimethyl acetal, 1.2 equiv of *N,N*-diisopropylethylamine, and dry dichloromethane (1.67 mL/mM of acetal) were combined under a nitrogen atmosphere and cooled to −20 °C, and trimethylsilyl triflate (1.1 equiv) was added dropwise. The reaction mixture was allowed to warm to ambient temperature and stirred for the times listed in Table I. Aqueous sodium hydroxide solution (1 M, 0.2 equiv) was added, and the reaction mixture was stirred vigorously for 5 min. The organic phase was separated, diluted with 2–3 volumes of pentane, and cooled overnight to precipitate the *N,N*-diisopropylethylammonium triflate. The liquid phase was removed, and the precipitate was washed with pentane. The solvent was removed from the combined liquid phases under reduced



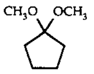
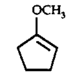
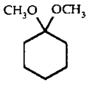
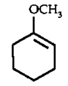
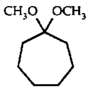
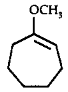
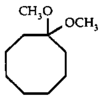
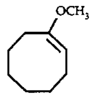
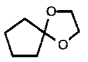
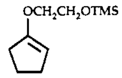
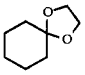
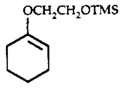
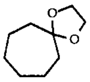
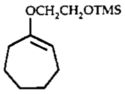
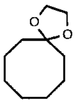
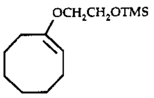
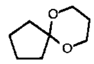
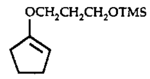
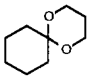
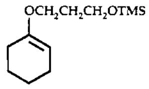
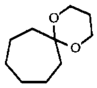
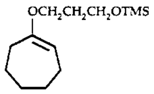
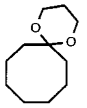
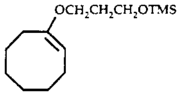
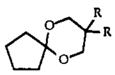
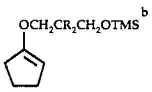
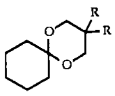
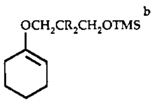
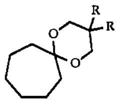
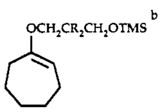
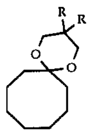
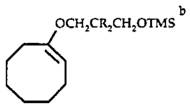
1
2

---

(1) Gassman, P. G.; Burns, S. J. *J. Org. Chem.*, following paper in this issue.
(2) For leading references, see: Wohl, R. A. *Synthesis* **1974**, 38. Cookson, R. C.; Singh, P. *J. Chem. Soc. C* **1971**, 1477. Schank, K.; Pack, W. *Chem. Ber.* **1969**, *102*, 1892. Lindsay, D. G.; Reese, C. B. *Tetrahedron* **1965**, *21*, 1673. Meerwin, H. In Houben-Weyl, *Methoden der Organische Chemie*; Muller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1965; Vol. 6/3, p 199ff.
(3) (a) Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1982**, *23*, 323. (b) Marsi, M.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1467. Marsi, M.; Gladysz, J. A. *Tetrahedron Lett.* **1982**, *23*, 631. Gladysz, J. A.; Williams, C.; Tam, W.; Johnson, D.; Parker, D.; Selover, J. *Inorg. Chem.* **1979**, *18*, 553. (c) Naruse, Y.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 1363.
(4) Mandai, T.; Hara, K.; Nakajima, T.; Kawada, M.; Otera, J. *Tetrahedron Lett.* **1983**, *24*, 4993. Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 5842. Mulzer, J.; Pointner, A.; Chuckolowski, A.; Bruntrup, G. *J. Chem. Soc., Chem. Commun.* **1979**, 52. Kluge, A. F. *Tetrahedron Lett.* **1978**, 3629. Julia, M.; Righini, A.; Uguen, D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1646.
(5) Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981**, *37*, 3899. Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357. See also: Hwu, J. R.; Wetzel, J. M. *J. Org. Chem.* **1985**, *50*, 3946.

0022-3263/88/1953-5574$01.50/0

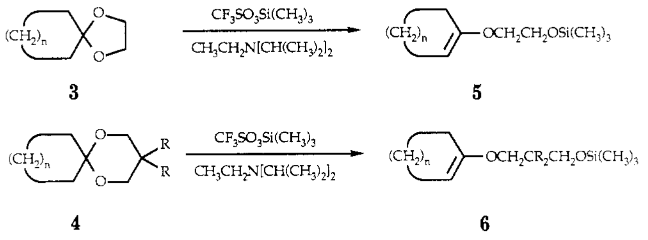
Table I. Conversion of Acetals to Enol Ethers with Trimethylsilyl Triflate-*N*,*N*-Diisopropylethylamine

reactant	product	TMSOTf, equiv	$CH_3CH_2N[CH(CH_3)_2]_2$, equiv	time, h	% yield
		1.1	1.2	2	95 (97)[a]
		1.1	1.2	3	94 (95)
		1.5	1.6	24	94 (98)
		1.1	1.2	4	91 (97)
		1.2	1.3	4	97 (99)
		1.2	1.3	4	94 (97)
		1.5	1.6	4	92 (98)
		1.2	1.3	4	98 (100)
		1.7	1.9	6	89 (96)
		1.7	1.9	22	95 (98)
		1.7	1.9	6	93 (97)
		1.7	1.9	22	90 (92)
		1.75	1.9	24	95 (95)
		1.75	1.9	72	93 (98)
		1.75	1.9	45	93 (97)
		1.75	1.9	36	94 (94)

[a] Small quantities of starting material remained in several reactions. Yields in parentheses are based on starting material consumed. [b] R = CH_3.

pressure, and the residue was distilled. For certain enol ethers, the distillate contained trace amounts of *N*,*N*-diisopropylethylamine. This impurity was removed by chromatography on a short basic alumina column with pentane as eluent. Redistillation afforded the yields of enol ethers, **2**, listed in Table I.

The conversion of cyclic ethers (1,3-dioxolanes, **3**, and 1,3-dioxanes, **4**) into enol ethers (**5** and **6**, respectively) was also investigated. In a general procedure, the cyclic acetal (1.00 equiv), *N,N*-diisopropylethylamine (1.35 equiv for **3**, 1.90 equiv for **4**), and dichloromethane (1.67 mL/mM of acetal) were combined and cooled to 0 °C under nitrogen, and trimethylsilyl triflate (1.20 equiv for **3**, 1.70 equiv for **4**) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for the time indicated in Table I. The reaction mixture was diluted with pentane (2–3 volumes) and cooled overnight to precipitate the *N,N*-diisopropylethylammonium triflate. The liquid phase was decanted, the precipitate was washed with pentane, the liquid phases were combined, and the solvent was removed under reduced pressure. Distillation of the residue gave the yields of enol ethers (**5** and **6**)[6] listed in Table I.

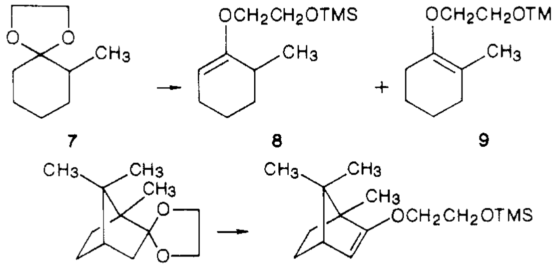


3 **5** **4** **6**

(a) R = H; (b) R = CH_3

In general, the yields of enol ethers were excellent. While the dimethyl acetals reacted rapidly, the dioxolanes were slightly less reactive, and the dioxanes were much less reactive. Thus, a larger molar ratio of trimethylsilyl triflate and a longer reaction period were used for the dioxanes. The dialkyl-substituted dioxanes were significantly less reactive than the simple dioxanes. For simple dimethyl acetals, the procedure described herein appears to give the best average yields of any available procedure.[7] For the dioxolanes and dioxanes, the previously published procedures either failed to give satisfactory yields in our hands[3a] or required experimental conditions that did not readily lend themselves to the preparation of large quantities of enol ethers in a simple laboratory procedure.

Two unsymmetrically substituted acetals were examined. When **7** was treated with trimethylsilyl triflate under the general procedure described above, a 96% yield of an 89:11 mixture of **8**:**9** was obtained based on 89% conversion of **7** after 5 h. This indicated that our procedure was more regioselective than procedures described earlier,[3] which tended to give ratios of **8** to **9** that approached the thermodynamic equilibrium mixture (63:37, respectively, for the methyl ethers).[8] When **10** was allowed to react under our general conditions for 18 h, except in refluxing methylene dichloride, a 91% yield of **11** was obtained. No rearrangement of the bornane skeleton was expected or observed. Thus, the procedure is applicable to molecules that tend to rearrange under cationic conditions.



7 **8** **9** **10** **11**

In conclusion, we have developed a simple, general, high-yield method for the preparation of enol ethers from acetals.

Acknowledgment. We are indebted to the National Science Foundation for a grant that supported this investigation.

---

[6] Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds. All products had IR, ^1H NMR, and ^{13}C NMR spectral data consistent with the assigned structures.

[7] Our yields are generally superior to those obtained by the procedure of Miller and McKean,[3a] which offers good yields of methyl vinyl ethers from dimethyl acetals.

[8] For the dimethyl acetal of 2-methylcyclohexanone, we obtained an 88:12 ratio of 1-methoxy-6-methylcyclohexene to 1-methoxy-2-methylcyclohexene.

Paul G. Gassman,* Stephen J. Burns
Department of Chemistry
University of Minnesota
Minneapolis, Minnesota 55455

Received May 31, 1988

Ring Expansions via Photoinduced Single Electron Transfer Promoted Opening of Cyclopropyl Ethers

Summary: A general method of ring expansion involving acetal to ring-homologated acetal is described. The key steps in the overall process involve (a) acetal to enol ether conversion, (b) cyclopropane formation, and (c) photoinduced single electron transfer promoted opening of the cyclopropane.

Sir: Recently, we have described a series of synthetically useful transformations of nonconjugated olefins, which were promoted by photoinduced single electron transfer reactions.[1-3] In principle, any molecule with an $E_{1/2}^{ox}$ less than 2.2 V vs a saturated calomel electrode (SCE) can be oxidized via single-electron transfer to an appropriate excited-state photosensitizer. The ease with which cyclopropyl ethers are oxidized (1.6–2.0 V vs SCE) suggested that a general process for acetal to acetal ring expansion might be possible involving (a) acetal to enol ether conversion,[4] (b) methylene addition to the enol ether to form a cyclopropyl ether, and (c) photochemical single electron transfer promoted cleavage of the cyclopropane and nucleophile capture by the intermediate cation radical to regenerate an acetal with a one-carbon homologation. We now report a series of examples of such homologations through, what we believe to be, the first examples of photoinduced single electron transfer promoted cleavages of simple nonconjugated cyclopropanes.

Our initial studies started with cyclic methyl enol ethers, **1**.[4] Cyclopropane formation from **1** was achieved with methylene iodide and zinc–copper couple in a standard Simmons–Smith reaction[5] to give **2** in yields ranging from 14 to 78%.[6] Irradiation of a methanolic solution that was

---

[1] Gassman, P. G.; Bottorff, K. *J. Am. Chem. Soc.* **1987**, *109*, 7547.

[2] Gassman, P. G.; Bottorff, K. *Tetrahedron Lett.* **1987**, *28*, 5449.

[3] Gassman, P. B.; Bottorff, K. *J. Org. Chem.* **1988**, *53*, 1097.

[4] For a general procedure for the conversion of acetals to enol ethers, see: Gassman, P. G.; Burns, S. J. *J. Org. Chem.*, preceding paper in this issue.

[5] Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React.* **1973**, *20*, 1.

0022-3263/88/1953-5576$01.50/0