products are thermally stable, efficient photoacid generators. The range of substituents surveyed resulted in materials that absorb light throughout the entire deep-UV and mid-UV range (220–350 nm), permitting their application for photoacid catalysis over a broad spectral range.

Experimental Section

Typical Procedure for the Preparation of Sulfonium Salts: Triphenylsulfonium Trifluoromethanesulfonate. A dry 50-mL flask was charged with phenyl sulfoxide (2.0 g, 9.9 mmol) along with freshly distilled methylene chloride (20 mL). The flask was cooled to −78 °C and treated dropwise with trimethylsilyl triflate (2.3 mL, 12 mmol) over 5 min. After the solution had been stirred for an additional 10 min at −78 °C, the flask was warmed to 0 °C and kept at that temperature for 30 min. The reaction mixture was recooled to −78 °C and treated dropwise with 10 mL of a 2.0 M (20 mmol) solution of phenylmagnesium chloride in THF. After an additional 30 min at −78 °C, the flask was warmed to 0 °C and kept at that temperature for 30 min. The reaction mixture was quenched with 3% aqueous triflic acid (30 mL) and diluted with ether (200 mL). The organic layer was washed with additional triflic acid (2 × 30 mL). The combined aqueous fractions were extracted with chloroform (3 × 30 mL), dried (Na_2SO_4), and concentrated to give 1.9 g (50%) of a white solid (recrystallized from butyl acetate/isopropyl alcohol, 3:1), mp 135–137 °C.[13]

Supplementary Material Available: Detailed spectral and analytical data are available (4 pages). Ordering information is given on any current masthead page.

A Study of the Sodium Borohydride Reduction of α,β-Acetylenic vs α,β-Olefinic Nitriles

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The conjugate reduction of α,β-acetylenic ketones to the corresponding α,β-ethylenic ketones was recently reported by Tsuda et al.[2] Earlier, we reported[3] the relative reactivities of α-arylcinnamonitriles with $NaBH_4$ in DMF. It seemed appropriate to extend this series to a conjugated acetylenic nitrile system, and phenylpropiolonitrile (1) was selected. Phenylpropiolonitrile has been reduced before, and there is conflicting information concerning its reaction with sodium borohydride.[4-6] Toda and Kanno[6] indicated the rapid formation of 3 at room temperature but Kadin[5] and Pepin[4] found that reduction of cinnamonitrile requires heating. We now present the kinetics for the sodium borohydride reduction of phenylpropiolonitrile (1), to cinnamonitrile (2), and β-phenylpropionitrile (3) (eq 1).

$$\underset{\mathbf{1}}{C_6H_5C{\equiv}CCN} \rightarrow \underset{\mathbf{2}}{C_6H_5CH{=}CHCN} \rightarrow \underset{\mathbf{3}}{C_6H_5CH_2CH_2CN} \quad (1)$$

All of the reductions were run in absolute ethanol at 25 or 0 °C. A summary of the kinetic results is listed in Table I.

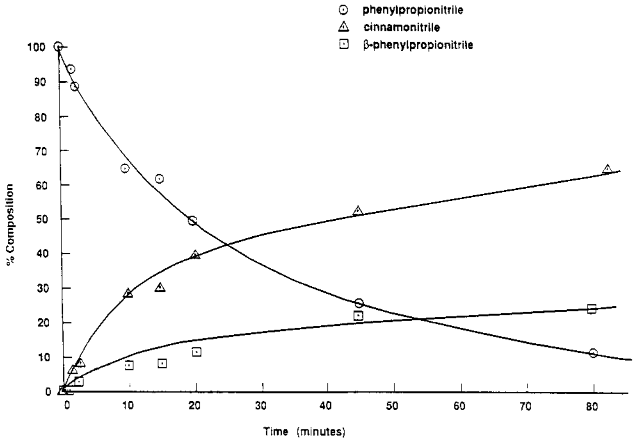

Figure 1. Reduction of 1 → 2 → 3 with $NaBH_4$/EtOH at 0 °C.

Table I. Half-Lives of Eight Reductions with $NaBH_4$/Absolute Ethanol

compound		temperature, °C	$t_{1/2}$, h	analytical method
$C_6H_5C{\equiv}CCN$	(1)	0	0.22	IR
	(1)	0	0.33	NMR
	(1)	25	too fast[a]	IR
$C_6H_5CH{=}CHCN$	(2)	0	270	IR
	(2)	0	370	NMR
	(2)	25	20[b]	IR
	(2)	25	20[c]	NMR
$C_6H_5CH{=}C(C_6H_5)CN$	(4)	25	3.6	IR

[a] Reaction complete in <10 min. [b] Correlation coefficient = 0.9993. [c] Correlation coefficient = 0.9998.

In comparing 1 and 2, it is estimated that the triple bond is reduced 1000 times faster than the corresponding double bond. Truce and co-workers[7] reported that the reduction of 1-mesityl-2-(mesitylsulfonyl)ethyne to its ethene derivative occurred at 0 °C, whereas the ethene to ethane transformation apparently required 50 °C and a longer reaction time for partial conversions in ca. 37% and 30% yields, respectively.

Starting with only phenylpropiolonitrile, the concentrations of this substrate (1) and of the mono- (2) and direduction products (3) found in the reaction mixture at various times are shown in Figure 1. The conditions were 0 °C and 0.2 M $NaBH_4$ in absolute ethanol. The aliquots were analyzed by the NMR technique.

Pepin,[4] in a competitive reaction experiment, found that after 35 min in boiling 2-propanol with an excess of $NaBH_4$, α-phenylcinnamonitrile (4) was completely reduced but only 10% of cinnamonitrile (2) was reduced. We have repeated this reaction under our conditions, and our results indicate that α-phenylcinnamonitrile is reduced ca. 6 times faster than cinnamonitrile. We cannot directly compare our results with those of Pepin[4] or with previous work[3] due to differences in experimental conditions and reference compounds. The IR method cannot be used for mixture analysis where there is another conjugated olefinic nitrile (2) or saturated nitrile present due to overlapping of C≡C and C≡N absorbances and the inability to distinguish unique peaks (see the Experimental Section). Consequently, the NMR procedure becomes the method of choice to analyze complex mixtures. However, the NMR calculations, based on integration ratios always totaling 100%, will appear to be more accurate than they are in fact.

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[1] Taken from the Senior Honors Paper of R.S., Moravian College, 1978.

[2] Tsuda, T.; Yoshida, T.; Kawamoto, T.; Saegusa, T. *J. Org. Chem.* **1987**, *52*, 1624.

[3] Kulp, S. S.; Caldwell, C. B. *J. Org. Chem.* **1980**, *45*, 171.

[4] Pepin, Y.; Nazemi, H.; Payette, D. *Can. J. Chem.* **1978**, *56*, 41.

[5] Kadin, S. B. *J. Org. Chem.* **1966**, *31*, 620.

[6] Toda, F.; Kanno, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2643.

[7] Truce, W. E.; Klein, H. G.; Kruse, R. B. *J. Am. Chem. Soc.* **1961**, *83*, 4636.

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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.

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(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.

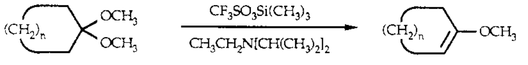
Communications

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

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(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