Table II. Values of K_1 and K_2 for Certain of the Complexes (CCl_4 Solvent, 25.0 °C)

donor	K_1, L mol^{-1}	K_2 L mol^{-1}
p-Bromanil Complexes		
cyclohexanone	1.01 ± 0.06	0.141 ± 0.006
tetrahydrofuran	0.75 ± 0.04	0.095 ± 0.004
N,N-diethylacetamide	2.89 ± 0.09	0.314 ± 0.010
N,N-dimethylacetamide	1.73 ± 0.17	0.19 ± 0.01
N-methylacetamide	0.87 ± 0.06	0.132 ± 0.012
N,N-dimethylformamide	1.06 ± 0.08	0.096 ± 0.008
δ-valerolactam	4.2 ± 0.05	0.63 ± 0.08
p-Fluoranil Complexes		
γ-butyrolactone	2.99 ± 0.15	0.31 ± 0.03
N,N-dimethylacetamide	7.67 ± 0.36	0.61 ± 0.04
N-methylacetamide	3.56 ± 0.21	0.44 ± 0.04
N,N-dimethylformamide	2.97 ± 0.04	0.21 ± 0.01
δ-valerolactam	8.54 ± 0.38	0.65 ± 0.05

Table II provides a summary of K_1 and K_2 values for *p*-bromanil complexes of certain of the donors for which K_c values are listed in Table I. These were evaluated from those Ketelaar plots of spectral data, which showed significant deviations from linearity in the region of high donor concentration. Table II also gives a summary of K_1 and K_2 values for certain *p*-fluoranil complexes that were not reported previously. In general, the relatively strong donors, the amides and lactams, provide readily apparent evidence of termolecular as well as bimolecular complex formation with *p*-bromanil. Cyclohexanone and tetrahydrofuran are included with those donors for which evidence of termolecular complex formation with this acceptor has been obtained. At first glance it may seem surprising that *p*-bromanil is as favorably disposed to undergo termolecular complex formation as it is. Actually a number of donors interact about as well with *p*-bromanil as with *p*-chloranil (see Table I). This is in keeping with the fact that the halogen atoms, bromine and chlorine, are not far apart in electronegativity, though they are substantially less electronegative than the fluorine atom.[8] Aside from possible steric problems, as discussed above, the differences in electronegatives of the halogens should be directly reflected to a considerable degree in the relative strengths of the three tetrahlobenzoquinones as acceptors.

(8) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.

Deoxygenation of Sulfoxides Promoted by Electrophilic Silicon Reagents: Preparation of Aryl-Substituted Sulfonium Salts

R. D. Miller,* A. F. Renaldo, and H. Ito*

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

Received May 17, 1988

The utility of substituted sulfonium salts in organic chemistry is manifested by the development of numerous synthetic routes to these materials.[1] Simple unhindered alkyl sulfonium salts are normally prepared by the direct alkylation of the corresponding sulfides by a wide variety of common alkylating reagents. Unfortunately, this technique is less successful for the preparation of sterically hindered or polyaryl-substituted materials.[1d] The preparation of sulfonium salts of this type usually requires the use of metallic complexing reagents[2] and/or the use of powerful electrophilic reagents.[3] The latter is epitomized by the sulfide arylation reaction, which requires the use of very electrophilic species such as aryl diazonium ions[4] or iodonium salts.[5] Recently, Julia and co-workers have reported the synthesis of a number of diphenyl alkyl substituted sulfonium salts by the alkylation of diphenyl sulfide with the corresponding alcohols in the presence of a variety of strong acids employed in excess.[6]

The recent discovery that triaryl-substituted sulfonium salts (Ar_3SMX_n) constitute a new class of thermally stable, nontoxic materials that produce protic acids upon irradiation has greatly stimulated interest in compounds of this type.[7] Synthetically, the direct addition of organometallic reagents to the corresponding diaryl sulfoxides followed by acidic hydrolysis constitutes perhaps the simplest and most straightforward route to triaryl sulfonium derivatives. In principle, this reaction was demonstrated by Wildi and co-workers,[8] although the procedure as described lacks generality, employs harsh reaction conditions that require large excesses of the organometallic reagents, and even under the best circumstances produces the desired sulfonium salts in mediocre yields. In addition, we have also recently discovered that it is unsuitable for the preparation of a number of unsymmetrical derivatives due to rapid ligand exchange under the reaction conditions.[9] The ligand exchange is exacerbated by the need for elevated temperatures and large excesses of Grignard reagent.

An alternative synthetic route has recently been reported by Crivello and Lam[10] which employs the thermal, copper-catalyzed, decomposition of aryl-substituted iodonium salts containing certain nonnucleophilic counterions in the presence of diphenyl sulfide.[10] This procedure, however, is multistep, requires the preparation and isolation of toxic iodonium salts, and fails in the presence of nucleophilic counterions.

The ready availability of sulfoxide starting materials makes the direct addition of organometallic reagents particularly attractive, provided the earlier difficulties can be overcome. For this, sulfoxide activation is essential to permit the addition to occur rapidly under mild reaction conditions, preferably with stoichiometric quantities of the organometallic reagents. In this regard, it has recently been demonstrated[11] that certain electrophilic silicon

(1) (a) *Comprehensive Organic Chemistry*; Barton, Ollis, W. D., Eds.; Pergamon: New York, 1979; Vol. 3, p 105ff. (b) *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum: New York, 1977. (c) *The Chemistry of the Sulfonium Group*, Sterling, C. J. M., Patai, S., Eds.; New York, 1981; Chapter 11. (d) *Sulfur Yields: Emerging Synthetic Intermediates*; Trost, B. M., Melvin, L. S., Jr., Eds.; Academic: New York, 1975; Chapter 2.

(2) (a) Franzen, V.; Schmidt, H. J.; Mertz, C. *Chem. Ber.* **1961**, *94*, 2942. (b) Frazen, V.; Driesen, H. E. *Ibid.* **1963**, *96*, 1881. Hashimoto, T.; Ohkubo, K.; Kitano, H., Fukui, K. *Nippon Kaguku Zasshi* **1966**, *87*, 456 and 1069.

(3) Tang, C. S. F.; Rapoport, H. *J. Org. Chem.* **1983**, *38*, 2806.

(4) Kobayashi, M.; Minato, H.; Fukui, J.; Kamigata, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 729.

(5) (a) Makarova, L. G.; Nesmeyanov, A. N. *Izv. Akad. Nauk SSSR* **1945**, 617. (b) Nesmeyanov, A. N.; Makarova, L. G.; Tolstaya, T. P. *Tetrahedron* **1957**, *1*, 145.

(6) (a) Badet, B.; Julia, M. *Tetrahedron Lett.* **1979**, 1101. (b) Badet, B.; Julia, M.; Lefebvre, C. *Bull. Soc. Chim. Fr.* **1984**, 11–431.

(7) (a) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Chem. Ed.* **1979**, *17*, 1059. (b) Crivello, J. V. *Chemtech.* **1980**, 624. (c) Perkins, W. C. *Rad. Curing* **1981**, *8*, 16. (d) Crivello, J. V.; Lam, J. H. W.; Volante, C. N. *Rad. Curing* **1977**, *4*(3), 2. (e) Pappas, P. S. *Prog. in Org. Coat.* **1985**, *13*, 35.

(8) Wildi, B. S.; Taylor, S. W.; Potratz, H. A. *J. Am. Chem. Soc.* **1951**, *73*, 1965.

(9) Ligand exchange upon reaction of organolithium compounds or Grignard reagents with aryl methyl sulfoxides has been reported previously: Kawai, T.; Furukawa, N.; Oae, S. *Tetrahedron Lett.* **1984**, *25*, 2549 and references cited therein.

(10) Crivello, J. V.; Lam, J. H. W. *J. Org. Chem.* **1978**, *43*, 3055.

0022-3263/88/1953-5571$01.50/0

reagents effect a rapid and facile deoxygenation of a number of sulfoxide derivatives, which suggested that reagents of this type might be useful for the preparation of sulfonium salts under mild reaction conditions when employed in conjunction with organometallic reactants. We have now demonstrated this to be the case and report here a simple and general procedure for the preparation of a variety of useful sulfonium salts.

The sulfonium salts (Table I) isolated by ether trituation of the concentrated chloroform extracts are usually pure enough for subsequent utilization. Further purification can be effected, if necessary, by recrystallization or by flash column chromatography on silica gel[12] with methylene chloride–10% methanol. Although we have chosen to describe mainly the preparation of the sulfonium triflates, the technique is not limited to this counterion. Other counterions can be introduced by varying the acid used upon quenching (entries 2, 6, 13). We have also demonstrated in one case that the corresponding bromide can be produced directly, albeit on lower yields, by employing trimethylsilyl bromide for activation (entry 2). Alternatively, the counterions can be interchanged by ion exchange with a basic exchange resin such as Amberlite IRA-400.[13]

As is evident from the data presented in Table I, the procedure is relatively general and can be used for the preparation of either triaryl or aryl alkyl substituted derivatives. In the latter cases (entries 12–15), we have concentrated on the preparation of materials that are difficult or impossible to prepare by direct alkylation and that require either the utilization of stoichiometric quantities of metal complexing reagents such as soluble silver salts or employ multistep synthetic sequences.[1d,14] In this regard, it is noteworthy that cyclopropyldiphenylsulfonium triflate (entry 12) was isolated in 64% yield, which compares favorably with the multistep synthesis of the corresponding tetrafluoroborate salt reported by Trost and Bogdanowciz.[15]

The use of electrophilic silicon reagents for activation results in the production of the sulfonium salts even when stoichiometric quantities of the organometallic reagent are used. For the triaryl derivatives where some excess of the organometallic reagent seems to cause no difficulties, we routinely employed a 20–100% excess of the reagent. However, for the preparation of mixed alkyl aryl derivatives where large excesses are detrimental, due to ligand exchange, stoichiometric quantities seem to give better yields. Preliminary experiments suggest that organolithium reagents can be substituted for the Grignard reagents (entry 3) at least in some cases. With the more reactive organolithium reagents, however, the sterically hindered silylation reagent *tert*-butyldimethylsilyl triflate is preferred. In the preparation of triphenylsulfonium triflate, the yield of product was significantly improved by the use of phenyllithium rather than phenylmagnesium bromide (entry 3). This result is interesting since it has been reported that the use of excess phenyllithium with no activating reagent produces little of the sulfonium salt[8,16] and results instead in significant fragmentation to phenyl sulfide and biphenyl.

Table I

$$Ph_2S{=}O + RMgBr \xrightarrow[(2)\ HX]{(1)\ R'SiMe_2OTf} RSPh_2X$$

Entry	R	R'	X⁻	Isolated Yield (%)[a]	MP °C (lit.)
1	phenyl-	methyl	Br[b]	26	285–287 (284–285)[8]
2	phenyl-	methyl	OTf	50	135–137[c]
3	phenyl-	t-butyl	OTf	75[d]	135–137[c]
4	phenyl-	methyl	OTf	40[d]	135–137[c]
5	p-styryl-	methyl	OTf	20[e]	f
6	p-styryl-	methyl	Br[g]	24	52–54 (dec.)
7	p-(trifluoromethyl)phenyl-	methyl	OTf	28	f
8	p-methoxyphenyl-	methyl	OTf	41	90–94
9	p-tolyl-	methyl	OTf	50	104–105[c]
10	4-(phenylthio)phenyl-	methyl	OTf	30	f
11	α-naphthyl-	methyl	OTf	44	135–138
12	cyclopropyl-	methyl	OTf	64	f
13	cyclobutyl-	methyl	BF_4[h]	48	94–95
14	isopropyl-	methyl	OTf	60	f[6]
15	isobutyl-	methyl	OTf	33	93–95

[a] Spectral data and elemental analyses are included in the supplementary material. [b] Trimethylsilyl bromide was used instead of trimethylsilyl triflate and the reaction was quenched with 5% hydrobromic acid. The temperature was maintained below −20 °C during the reaction and workup. [c] This compound is described in ref 13 but no melting point is given. [d] One equivalent of phenyllithium was used instead of excess Grignard reagent. [e] This sulfonium salt polymerized upon standing at 0 °C. [f] Isolated as a viscous oil. [g] Prepared by quenching the reaction mixture with 5% hydrobromic acid. [h] The tetrafluoroborate salt was found to be more stable than the corresponding triflate, which decomposed slowly at 0 °C.

Although the yields of this reaction are moderate, those reported in Table I are for the purified, isolated products. In some cases, the crude yield of product was much higher. This was particularly apparent for the styrenyl derivatives (entries 5 and 6) where the sulfonium salt was quite prone to polymerization upon purification.

The isolation of the unsymmetrical sulfonium salts (entries 5–15) by this technique is particularly significant. In our hands, the attempted preparation of *p*-tolyldiphenylsulfonium salts by the Wildi procedure[8] led to rapid ligand exchange and the isolation of impure product containing more than one *p*-tolyl substituent as determined by proton and carbon NMR analysis. However, no evidence of ligand exchange was apparent in the isolated sulfonium salts when the reaction was run in the presence of silyl triflates.[17] In addition, the preparation of unsymmetrical derivatives containing polynuclear aromatic substituents by this procedure is possible (entry 11), although the workup procedure becomes somewhat more complicated when the sulfonium salt is not readily soluble in aqueous acid.

In summary, we have described a simple one-step synthesis of both symmetrically and unsymmetrically substituted sulfonium salts. The reaction is rapid and reasonably substituent tolerant, and the products are isolated in a high state of purity. It is equally applicable to both large- and small-scale preparations and requires only a small stoichiometric excess of the organometallic reagent. No evidence of ligand exchange was observed in the preparation of unsymmetrical derivatives. Most of the

(11) (a) Olah, G. A.; Balaram Gupta, B. G.; Narang, S. C. *Synthesis* **1977**, 583 and references cited therein. (b) Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1983**, *24*, 2619. (c) Miller, R. D.; Hassig, R. *Tetrahedron Lett.* **1985**, *26*, 2395. (d) Miller, R. D.; Hassig, R. *Synth. Commun.* **1985**, *14*, 1285. (e) Lane, S.; Quick, S. J.; Taylor, R. J. K. *Tetrahedron Lett.* **1984**, *25*, 1039.

(12) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(13) Okamoto, T.; Endo, Y.; Shudo, K. *Chem. Pharm. Bull.* **1981**, *29*, 3753.

(14) The preparation of the cyclobutyldiphenylsulfonium tetrafluoroborate is particularly interesting, and we are currently investigating the chemistry of the ylide formed from this material.

(15) Trost, B. M.; Bogdanowciz, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 3773.

(16) Andersen, K. K.; Yeager, S. A. *J. Org. Chem.* **1963**, *28*, 865.

(17) Unsymmetrical triarylsulfonium salts have also been reported from the reaction of diarylethoxysulfonium salts with aryl Grignard reagents. Andersen, K. K.; Papanikolaou, N. E. *Tetrahedron Lett.* **1966**, 5445.

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

Stuart S. Kulp* and Richard Szarko[1]

Chemistry Department, Moravian College, Bethlehem, Pennsylvania 18018

Received April 15, 1988

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.

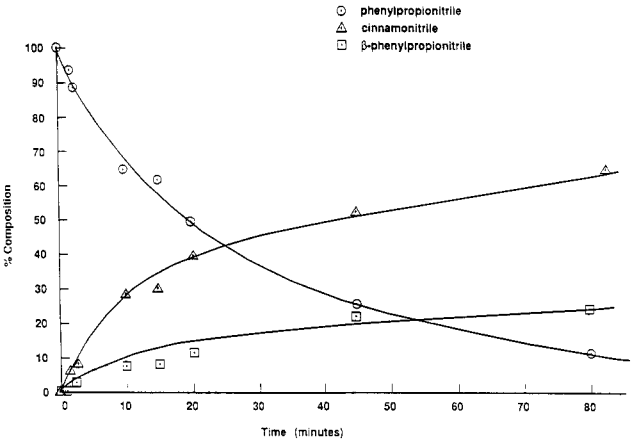

Figure 1. Reduction of **1** → **2** → **3** with $NaBH_4$/EtOH at 0 °C.

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.

(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.

0022-3263/88/1953-5573$01.50/0