Heteroatom Chemistry
Volume 15, Number 3, 2004

Application of Alkoxy-λ⁶-sulfanenitriles as Strong Alkylating Reagents

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Received 12 December 2003; revised 15 December 2003

ABSTRACT: *Alkoxy-λ⁶-sulfanenitriles were found to be versatile alkylating reagents toward various nucleophiles bearing at least one proton such as methanol, phenol, thiophenols, carboxylic acids,* p-*toluenesulfonic acid, hydrochloric acid, and primary and secondary amines. Reactivity of the alkoxy group of the λ⁶-sulfanenitriles showed an opposite trend to the usual S_N2 character, i.e. Me (***1a***), Pr (***1b***), and Bu (***1d***) ≪* i-*Pr (***1c***). In the presence of* p-*TsOH, alkyl tosylates were predominantly formed instead of the alkylation products of nucleophiles. In addition, even a sterically hindered substrate, neopentyloxy-λ⁶-sulfanenitrile, was found to undergo an S_N2 reaction toward thiophenol without any rearrangement product to give neopentyl phenyl sulfide in good yield.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:193–198, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20006

INTRODUCTION

λ⁶-Sulfanenitriles (thiazynes) [1a,1b] are relatively unusual compounds bearing a sulfur-nitrogen triple bond and three ligands on the sulfur atom. Only a few inorganic λ⁶-sulfanenitriles, such as F_3SN, are known and their chemistry has been developed by Glemser et al. [2] in the field of inorganic or fluorine chemistry. Meanwhile, we have explored the chemistry of organic λ⁶-sulfanenitriles since our first preparation of methoxydiphenyl-λ⁶-sulfanenitrile in 1989 [3] without use of trifluoro-λ⁶-sulfanenitrile as the starting material.

In recent years, we have prepared a series of organic λ⁶-sulfanenitriles [4,5], and have reported the X-ray structural analysis of some λ⁶-sulfanenitriles [4c,4d,5]. In our previous paper [5], it was reported that alkoxy-λ⁶-sulfanenitriles [5] exceptionally undergo a facile Ei reaction, although λ⁶-sulfanenitriles are tetracoordinated hexavalent sulfur compounds like sulfones and sulfoximides. Furthermore, during the synthesis and the assignment of the structure of these alkoxy-λ⁶-sulfanenitriles [5,6], it was found that they undergo acid-catalyzed hydrolysis readily, even under slightly alkaline conditions, to yield the corresponding sulfoximide [2] and alcohols. Moreover, we reported that methoxydiphenyl-λ⁶-sulfanenitrile reacts with thiols to give methyl sulfides and diphenyl sulfoximide, and clarified the mechanism that involves an initial equilibrated protonation of the λ⁶-sulfanenitrile by thiols followed by nucleophilic attack of the thiolate anions on the methyl group in the rate-determining step [7]. Both the acid-catalyzed hydrolysis and the reaction with thiols show that the sulfoximide moiety of protonated alkoxy-λ⁶-sulfanenitriles is a very good leaving group and thus alkoxy-λ⁶-sulfanenitriles are very effective alkylating reagents. As an application of this reaction, the scope and limitations of the use

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Contract grant sponsor: Ministry of Education, Culture, Sports, Science and Technology.
Contract grant numbers: 13029039 and 14044032.

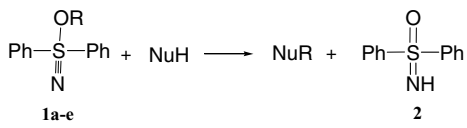
of alkoxy-λ⁶-sulfanenitriles as alkylating agents were examined.

RESULTS AND DISCUSSION

Reaction of Alkoxy-λ⁶-sulfanenitriles with Various Nucleophiles

In order to study these alkylation reactions for various nucleophilic agents, the alkylation reaction of various nucleophiles with these alkoxy-λ⁶-sulfanenitriles was carried out in an NMR tube. The products were identified by comparing their IR and NMR spectra with those of the authentic samples or the reported data. These alkoxy-λ⁶-sulfanenitriles gave the corresponding alkylation products in high yields toward oxygen (alcohol, carboxylic, sulfonic acids), nitrogen (amines), and sulfur (thiols) nucleophiles, as shown in Scheme 1 and Tables 1–3.

Alcohols were relatively hard to be alkylated in chloroform. But the reaction of isopropoxy-λ⁶-sulfanenitrile (**1c**) with MeOH as solvent afforded



1a-e **2**

(**1a**: R = Me, **1b**: R = Pr, **1c**: R = ^{i}Pr, **1d**: R = Bu, **1e**: R = Neopentyl)

SCHEME 1

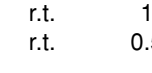
isopropyl methyl ether quantitatively. Meanwhile, phenol and thiols were more easily alkylated than alcohols. The reaction of the alkoxy-λ⁶-sulfanenitriles with primary and secondary amines also gave the corresponding *N*-alkylated amines. Structural effect of the alkyl group showed an opposite trend to the usual S_N2 character, i.e., primary (**1a, 1b, 1d**) ≪ secondary (**1c**), as shown in the reaction with phenol. This tendency is the same as the kinetic results in the hydrolysis we reported previously [6]. Meanwhile, methyl phenyl sulfide and Et_3N as nucleophiles could not be alkylated, so that an active proton on the reagents is required for

TABLE 1 Alkylation Products by Reactions of Alkoxy-λ⁶-sulfanenitriles[a] with Nucleophiles

Substrates	*Nucleophile*		*Conditions*			*Products Yield (%)*[b]	
1a–d *(R)*	*NuH*	*Eq.*	*Temp (°C)*	*Time*	*Solvent*	*NuR*	*(**2**)*
1a (Me)	PhSH	2.0∼3.0	30	10 h	C_6H_6	95	96[c]
	$PhSCH_3$	2.0∼3.0	50	3 days	$CHCl_3$	0	0[c]
1b (Pr)	CH_3OH	20	r.t.	72 h	$CDCl_3$	0	1
	CH_3OH	20	45	114 h	CH_3OH	0	3
	PhOH	2.0	r.t.	336 h (78 h)	$CDCl_3$	89 (15)	91 (16)
	PhSH	1.3	r.t.	2 h	$CDCl_3$	99	99
	$ClC_6H_4CH_2NH_2$	80	40	24 h	$ClC_6H_4CH_2NH_2$	20	22
	Piperidine	85	40	24 h	Piperidine	96	98
	Alanine	2.0	40	50 h	CD_3CN	0	0
	AcOH	1.3	r.t.	15 min	$CDCl_3$	89	92
	CF_3COOH	1.0	r.t.	1 h	$CDCl_3$	99	99
	p-TsOH	1.3	r.t.	1 h	$CDCl_3$	98	99
	HCl	1.5	r.t.	0.5 h	CD_3CN	98	99
1c (*i*-Pr)	CH_3OH	20	r.t.	19 h	$CDCl_3$	18	20
	CH_3OH	20	45	114 h	CH_3OH	99	99
	CD_3OD	200	r.t.	2 h	CD_3OD	99	99
	PhOH	2.0	r.t.	78 h	$CDCl_3$	98	99
	PhSH	1.3	r.t.	2 h	$CDCl_3$	99	99
	$ClC_6H_4CH_2NH_2$	80	40	24 h	$ClC_6H_4CH_2NH_2$	95	97
	Piperidine	85	40	24 h	Piperidine	69	75
	Alanine	2.0	40	50 h	CD_3CN	0	0
	Et_3N	2.0	40	72 h	$CDCl_3$	0	0
	AcOH	1.3	r.t.	5 min	$CDCl_3$	99	99
	p-TsOH	1.3	r.t.	15 min	$CDCl_3$	99	99
	HCl	1.5	r.t.	15 min	CD_3CN	99	99
1d (Bu)	PhOH	2.0	r.t.	336 h (78 h)	$CDCl_3$	91 (16)	92 (17)
	AcOH	1.3	r.t.	15 min	$CDCl_3$	99	99

[a]Substrates.
[b]The yields and purity were determined by ^{1}H NMR analysis.
[c]Ref. [7].

TABLE 2 Alkylation Products by Reactions of Alkoxy-λ^6-sulfanenitrile[a] with Nucleophiles in the Presence of Acid

Substrates	*Nucleophile*		*Conditions*				*Products and Yield (%)*[b]		
1b,c *(R)*	*NuH*	*Eq.*	*Temp.*	*Time (h)*	*Acid (eq).*	*Solvent*	*NuR*	(**2**)	*Others*
1b (Pr)	PhOH	2.0	r.t.	24	*p*-Ts OH (1.0)	$CDCl_3$	12	99	*p*-TsOPr (71)
1c (*i*-Pr)	Menthol	2.0	r.t.	0.5	*p*-Ts OH (1.0)	$CDCl_3$	0	99	*p*-TsO-*i*-Pr (99)
1b (Pr)	Geraniol	2.0	r.t.	1	*p*-Ts OH (1.0)	$CDCl_3$	0	99	*p*-TsOPr (99)
1c (*i*-Pr)	Piperidine	1.0	r.t.	0.5	 (1.0)	CD_3CN	0	99	*p*-TsO-*i*-Pr (99)
1b (Pr)	Benzylamine	1.0	r.t.	1	$PhCH_2\overset{+}{N}H_3\ \overset{-}{O}Ts$ (1.0)	CD_3CN	0	99	*p*-TsOPr (99)

[a]Substrates.
[b]The yields and purity were determined by ^{1}H NMR analysis.

these reactions. We have reported the importance of the initial protonation of the nitrogen atom of alkoxy-λ^6-sulfanenitriles in both the hydrolysis and the reaction of methoxy-λ^6-sulfanenitrile with thiols [7]. Therefore, the alkylations were examined under acid-catalyzed conditions.

Unexpectedly, the presence of acid was found to reduce the yield of the alkylation products (Table 2). In the presence of *p*-toluenesulfonic acid in $CDCl_3$, phenol was alkylated in a rather lower yield, and menthol and geraniol were not alkylated at all, while *p*-TsOH was instead alkylated quantitatively. Piperidine and benzylamine in the presence of their *p*-toluenesulfonate salts did not afford the alkylated amines but gave alkyl *p*-toluenesulfonates. Interestingly, even weaker nucleophiles, anions of the stronger acid, showed a higher reactivity than the neutral stronger nucleophiles.

Then the reactions of compound **1** with acetic, trifluoroacetic, *p*-toluenesulfonic, and hydrochloric acids were carried out in $CDCl_3$. As shown in Table 1, even a strong acid, whose conjugate base is a very weak nucleophile, *p*-TsOH, gave the corresponding ester quantitatively. These reactions reveal that

TABLE 3 Reactions of Neopentyloxy-λ^6-sulfanenitrile (**1e**)[a] with Nucleophiles

Nucleophile			*Conditions*			*Products Yield (%)*[b]		
Entry	*NuH*	*Eq.*	*Time*	*Temp. (°C)*	*Solvent*	$NuCH_2C(CH_3)_3$	(**2**)	*Others*
1	CH_3OH	20	24 h	r.t.	$CDCl_3$	0	1	–
2	CH_3OH	65	114 h	45	CH_3OH	0	2	–
3	*p*-TolOH	2.0	240 h	r.t.	$CDCl_3$	0	1	–
4	*p*-TolOH	56	114 h	45	*p*-TolOH	0	98	–[c]
5	PhOH	2.0	144 h	r.t.	$CDCl_3$	0	3	–
6	PhOH	61	114 h	45	PhOH	0	99	–[c]
7	PhOH	2.0	1 h	r.t.	$CDCl_3(H^+)$[d]	Trace[e]	99	–[c]
8	PhSH	1.3	8 h	40	$CDCl_3$	98[f]	99	–
9	PhSH	1.3	8 h	40	$CDCl_3(H^+)$[g]	85[f]	88	–
10	AcOH	5.0	2 h	r.t.	AcOH	0	99	–[c]
11	*p*-TsOH	1.3	48 h	r.t.	$CDCl_3$	12	99	–[c]
12	$ClC_6H_4CH_2NH_2$	80	24 h	40	$ClC_6H_4CH_2NH_2$	0	6	10[h]
13	$ClC_6H_4CH_2NH_2$	80	114 h	45	$ClC_6H_4CH_2NH_2$	0	15	67[h]
14	Piperidine	85	24 h	40	Piperidine	0	20	$(CH_3)_3CCH{=}O$ (18)
15	Piperidine	85	114 h	45	Piperidine	0	43	$(CH_3)_3CCH{=}O$ (49)
16	Alanine	2	50 h	40	CD_3CN	0	1	–

[a]Substrate.
[b]Yields and purity were determined by ^{1}H NMR analysis.
[c]Complex mixture of rearranged products ($NuC(CH_3)_2CH_2CH_3$, $CH_3CH{=}C(CH_3)_2$, $CH_3CH_2C(CH_3){=}CH_2$, etc.).
[d]0.05 eq. *p*-TsOH.
[e]$TsOCH_2C(CH_3)_3$.
[f]Ref. [8].
[g]0.06 eq. *p*-TsOH.
[h]$ClC_6H_4CH_2N{=}CHC(CH_3)_3$.

alkoxy-λ⁶-sulfanenitriles serve as strong alkylating agents toward acids and actual nucleophiles are their conjugate bases. However, in the case of the reaction with piperidine and *p*-chlorobenzylamine, the proton transfer from the amines to the nitrogen atom of the λ⁶-sulfanenitrile is unlikely because of too much difference of the pK_a values between the protonated λ⁶-sulfanenitriles and the unprotonated amines. The reactions with piperidine and *p*-chlorobenzylamine may proceed by their direct attack or by a general base catalysis.

From these findings, it is suggested that the reactivity depends on both the position of the equilibrium of the initial protonation and the nucleophilicity of the counter anion. The fact that alanine is not alkylated may be interpreted as follows. In the second step the reaction involves the protonated cation of the λ⁶-sulfanenitrile and the carboxylate counter anion whose nucleophilicity is similar to acetate anion. But the initial equilibrium constant is considered to be much smaller than that of acetic acid from the pK_a difference between alanine (pK_a = 9.69) and acetic acid (pK_a = 4.8). Thus the reaction with alanine must be very slow.

*Reaction of Neopentyloxydiphenyl-λ⁶-sulfanenitrile (**1e**) with Various Nucleophiles*

Since the structural effect of the alkoxy group shows an opposite trend to the usual S_N2 reaction, it is interesting to examine how this reaction overcomes the steric effect. As a sterically hindered alkoxy derivative, neopentyloxy(diphenyl)-λ⁶-sulfanenitrile (**1e**) was examined as the alkylating agent (Table 3).

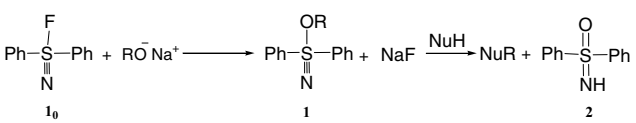
It is interesting that the reaction of **1e** with thiophenol gave neopentyl phenyl sulfide in good yield without any rearrangement (entry 8), since there are only a few examples of substitution reaction on the neopentyl carbon atom. The presence of *p*-toluenesulfonic acid only lowered the yield like other alkoxy-λ⁶-sulfanenitriles (entry 9). The reaction with *p*-TsOH in $CDCl_3$ at room temperature also afforded neopentyl tosylate in 12% yield together with a complex mixture of rearranged products which are considered to be formed via rearrangement of neopentyl cation (entry 11). However, the reaction with methanol, *p*-cresol, and phenol at room temperature did not afford any product without rearrangement (entries 1, 3, and 5). The reaction with phenol in the presence of *p*-TsOH in $CDCl_3$ gave a trace amount of neopentyl tosylate and the similar complex mixture (entry 7). On the other hand, the reaction with piperidine and *p*-chlorobenzylamine without solvents by warming did not afford the corresponding neopentylamines, but afforded thermal decomposition product 2,2-dimethylpropanal (entries 14 and 15) and its condensation product 2,2-dimethylpropylidene-*p*-chlorobenzylamine (entries 12 and 13), respectively. However, the reaction with phenol, *p*-cresol, and AcOH afforded only complex rearranged products and no Ei products even at 45°C (entries 6, 4, and 10). We reported previously that alkoxy-λ⁶-sulfanenitriles undergo facile Ei reaction in refluxing benzene to afford the corresponding elimination products and *N*-unsubstituted diphenylsulfilimine [5]. Ei reactions of sulfoxides and sulfilimines in protic solvents are known to undergo rate retardation [9,10], which is attributable to the result of no Ei reaction of **1e** in phenol and *p*-cresol.

One-Pot Reaction

One-pot alkylation of nucleophiles by sodium alkoxide using fluoro(diphenyl)-λ⁶-sulfanenitrile was also carried out. Alcohols were first converted to sodium alkoxide in DMSO (method A) or alcohols (method B) using sodium hydride or metallic sodium, respectively, and to this was added fluorodiphenyl-λ⁶-sulfanenitrile to give the corresponding alkoxy-λ⁶-sulfanenitriles and then various nucleophilic reagents (NuH) to afford the corresponding alkylation products (Scheme 2). These methods are effective to avoid the accompanying hydrolysis of alkoxy-λ⁶-sulfanenitriles during their separation. As some examples shown in Table 4, PhSH, AcOH, and *p*-TsOH were successfully alkylated in good yields. The one-pot reaction is especially useful to obtain an acid ester of inverted alcohols like the Mitsunobu reaction [11–13].

Discussion

According to our previous mechanistic investigation of the hydrolysis of alkoxy(aryl)(phenyl)-λ⁶-sulfanenitriles and the reaction of methoxydiphenyl-λ⁶-sulfanenitrile with thiols [6,7], the present reaction is considered to proceed via an initial protonation of the nitrogen atom of the alkoxy-λ⁶-sulfanenitrile by the conjugate acid (NuH) of the nucleophiles (Nu^-) followed by a nucleophilic attack of the counter anions at the alkoxy carbon probably



SCHEME 2

TABLE 4 Alkylation Products from Diphenylfluoro-λ⁶-sulfanenitrile[a]

Substrate	*Nucleophile*				*Conditions*			*Products and Yield (%)*[b]	
1_0	*(1)RO^- Na^+*	*Eq.*	*(2) NuH*	*Eq.*	*Method*	*Temp (°C)*	*Time*	*NuR*	(**2**)
	^{i}PrO$^-$ Na$^+$	1.1	PhSH	1.3	A	r.t.	2 h	78	83
$Ph_2S(F)N$	^{i}PrO$^-$ Na$^+$	1.1	AcOH	1.3	B	r.t.	10 min	86	90
	^{i}PrO$^-$ Na$^+$	1.1	*p*-TsOH	1.3	B	r.t.	20 min	88	93

[a]Substrate.
[b]The yields and purity were determined by ^{1}H NMR analysis.

through an S_N2 transition state. The opposite trend of the structural effect of the alkyl group shows a carbocation-like loose transition state like their hydrolysis mechanisms [6]. The tendency that the more acidic conjugate acids are more reactive suggests that the initial protonation is more important than the next step as reported previously [7]. The exclusive formation of the alkyl tosylate from the alkylamine in the reaction of isopropoxy-λ⁶-sulfanenitrile with piperidine in the presence of piperidinium tosylate suggests that the counter anion is more nucleophilic than the amine in an organic solvent, probably because of stronger ion-pair interaction than ion-molecule interaction in the second step nucleophilic reaction.

The present reaction is similar to esterification of carboxylic acids by diazomethane in view of involvement of the initial protonation and the following facile alkylation. But the present system is available to a wide variety of alkylation and is safer. Our method is also similar to the Mitsunobu reaction [11–13], because alcohols are first activated and various nucleophiles having an active proton can easily be alkylated at the second step. Though the yield of the alkylation of alcohols using primary alkoxy-λ⁶-sulfanenitriles is low compared to the Mitsunobu reaction, the alkylation of even strong acids is an important feature at the present reaction.

EXPERIMENTAL

Reagents and Instruments

Reagents and solvents were obtained commercially and were further purified by general methods when necessary. IR spectra were taken on a Horiba FT-710 spectrometer, ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL-JNM 400 NMR spectrameter in $CDCl_3$, CD_3CN, or CD_3OD with TMS as an internal standard. Elemental analyses were performed on a Yanaco MT-5 CHN CORDER. Fluoro- and alkoxy-λ⁶-sulfanenitriles were prepared according to the methods reported in our previous papers [5,6].

Alkylation of Various Nucleophiles with Alkoxy-λ⁶-sulfanenitriles

A typical example is as follows: to a 5-ml solution of alkoxydiphenyl-λ⁶-sulfanenitrile (ca. 7.0×10^{-3} mol dm^{-3}) in $CDCl_3$, CD_3CN, CD_3OD, or no solvent in an NMR tube, was added an appropriate amount of nucleophile, and ^{1}H NMR was taken immediately and at appropriate time intervals. After ^{1}H NMR signals of the alkoxy-λ⁶-sulfanenitriles disappeared or showed no further change, the products were analyzed by comparing their IR and NMR spectra with those of the authentic samples or the reported data. The yields of the products were determined by ^{1}H NMR from the integral ratios of the products to the sum of **2** and the alkoxy-λ⁶-sulfanenitriles as shown in Tables 1–3. The by-product *S,S*-diphenylsulfoximide (**2**) was obtained in almost quantitative yield.

One-Pot Reaction

Method A. A typical example is as follows: to a 30-ml Erlenmeyer flask was added 100 mg (2.3 mmol) of 55% dispersion of sodium hydride in mineral oil. The sodium hydride was washed several times by decantation with dry ether. To this was added 6 ml of DMSO to dissolve sodium hydride with stirring at room temperature under an argon atmosphere. After 1 h, 0.2 ml (2.6 mmol) of dry isopropanol was added into the reaction solution and was allowed to react by stirring for 1 h to give a sodium alkoxide solution. A solution of fluorodiphenyl-λ⁶-sulfanenitrile **1_0** (438 mg, 2 mmol) in DMSO (6 ml) was added to the stirred solution of sodium alkoxide. After stirring for 10 min, 0.268 ml (2.6 mmol) of thiophenol was added and stirring was continued for 2 h. The reaction mixture was poured into ice water and extracted with chloroform (5×5 ml). The combined organic extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give isopropyl phenyl sulfide in 78% yield and *S,S*-diphenylsulfoximide (**2**) as

shown in Table 4. The products were identified by comparing their IR and NMR spectra with those of the authentic samples.

Method B. Typical examples are as follows: to a 30 ml Erlenmeyer flask was added 26 mg (1.1 mmol) of sodium and 8 ml dry isopropanol to dissolve the all metallic sodium. To this was added fluorodiphenyl-λ^6-sulfanenitrile $\mathbf{1_0}$ (219 mg, 1 mmol) in 8 ml of dry isopropanol at room temperature under an argon atmosphere. After stirring for 10 min, the reaction mixture was condensed to afford a slurry which was dissolved in 2 ml of $CDCl_3$. The supernatant was decanted to 0.075 ml (1.3 mmol) of AcOH or 224 mg (1.3 mmol) of *p*-TsOH for 10 min or 15 min, respectively, to give the corresponding isopropyl ester and *S,S*-diphenylsulfoximide (**2**) as shown in Table 4.

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