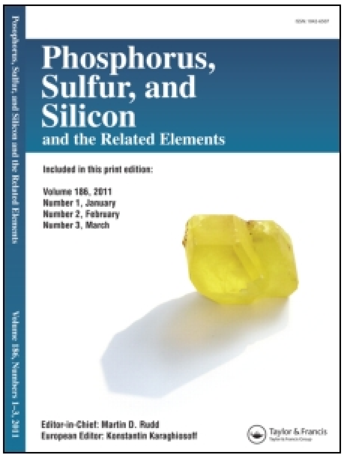

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THE SULFUR (11)-NITROGEN BOND. PART IV[1]. AMINOSULFENATES

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THE SULFUR (11)-NITROGEN BOND. PART IV[1]. AMINOSULFENATES

by

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ABSTRACT

Aminosulfenates R_2NSOR' have been prepared from aminosulfenyl chlorides and tin alkoxides. They form sulfenyl chlorides with chlorosilanes, bisamino-sulfides with secondary amines and polysulfides with thiols.

Esters of sulfenic acids are normally prepared from the sulfenyl chloride using a slurry of the sodium alkoxide in an inert solvent.[2] This method has two inherent practical disadvantages in that the sodium alkoxide has to be alcohol free, and the products should be filtered prior to fractionation. Tin amines have been used widely as aminating agents,[3] but tin alkoxides have not been studied much with a view to using them for alkoxylation, except for the Group IV elements.[4]

Results and Discussion

In this paper we report the synthesis of benzene sulfenates from the chloride and tin alkoxide, and the extension of the method to prepare aminosulfenates R_2NSOR', a new class of compound isomeric with sulfinamides $R_2NS(O)R'$.

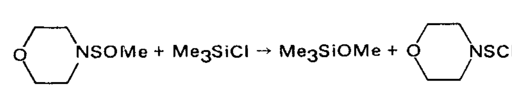
Benzenesulfenyl chloride reacts exothermically with tri-*n*-butyltin methoxide, with the formation of colorless products. O-Methyl benzenesulfenate can be readily distilled from the product mixture and in excellent yield.

$$Bu_3{}^nSnOMe + PhSCl \rightarrow PhSOMe + Bu_3{}^nSnCl$$

Yellow aminosulfenyl chlorides, prepared from the bisaminosulfide and sulfur dichloride,[5] discolorize upon reaction with an excess of the tin alkoxide and vacuum distillation of the resulting mixture gives the aminosulfenates in good yield as colorless liquids.

$$Me_2NSCl + Bu_3{}^nSnOR \rightarrow Me_2NSOR + Bu_3{}^nSnCl$$
$$(R = Me, Et, Pr^n, Bu^n)$$
$$R_2NSCl + Bu_3{}^nSnOMe \rightarrow R_2NSOMe + Bu_3{}^nSnCl$$
$$(R_2N = Et_2N, Pr_2{}^nN, \text{morpholino})$$

The aminosulfenyl chlorides can be regenerated from the aminosulfenate using a chlorosilane. This indicates that S–Cl and S–O probably have



similar bond strengths, as the differences between Sn–Cl and Sn–OEt and between Si–OEt and Si–Cl are 9 and 7 kcal/mole respectively.[6]

Sulfenate esters are cleaved at the S–O bond by both amines and thiols, giving sulfenamides and disulfides.[1,7] Aminosulfenates react similarly. Thus, bis(diethylamino)sulfide results from diethylamine and the appropriate O-methyl aminosulfenate.

$$Et_2NH + Et_2NSOMe \rightarrow (Et_2N)_2S + MeOH$$

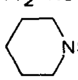
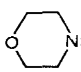
Ethane thiol attacks both the S–O and S–N bonds of O-*n*-propyl dimethylaminosulfenate but the generation of basic dimethylamine precludes the formation of a good yield of diethyltrisulfide. A small amount was isolated but the major product of the reaction was diethyldisulfide, formed from the trisulfide in the presence of base.[8]

$$Me_2NSOPr^n \xrightarrow{\text{excess EtSH}} Et_2S_3 \xrightarrow{\text{base}} Et_2S_2$$

Experimental Section

All reactions were carried out under strictly anhydrous conditions, with cooling where necessary. Benzenesulfenyl chloride[9] and the various aminosulfenyl chlorides[5] were prepared as reported. These compounds tend to decompose readily so are difficult to analyze and have to be used promptly. Their properties are summarized in Table I.

TABLE I
Aminosulfenyl Chlorides

	bp (°C/mm)	n_D^{24}
Me_2NSCl	41/16	1.5145
Et_2NSCl	38/3	1.5073
Pr_2^nNSCl	45/0.01	1.4956
NSCl	53/0.2	1.5470
NSCl	56/0.4	1.5492

The Reaction of Benzenesulfenyl Chloride and Tri-n-butyltin Methoxide

The red chloride (4.82g., 1 mol) was added dropwise to the methoxide (10.7 g, 1 mol) with cooling. Immediate discoloration occurred, and after leaving stirring for 2 hr., vacuum distillation yielded O-methyl benzenesulfenate, bp 34°/0.1 mm., n_D^{25} 1.5619 (3.1 g, 66%) and tri-*n*-butyltin chloride, bp 78°/0.01 mm., n_D^{25} 1.4940 (7.5 g, 70%).

The Reaction of Aminosulfenyl Chlorides with Tri-n-butyltin Alkoxides

Morpholinosulfenyl chloride (7.8 g, 1 mol) was added dropwise to tri-*n*-butyltin methoxide (19.0 g, 1.1 mol) with cooling. The mixture was stirred and warmed for 1 hr and subsequent vacuum distillation yielded the aminosulfenate (6.7 g, 84%), bp 42°/0.8 mm., n_D^{24} 1.4861

Anal. Calc. for $C_5H_{11}NSO_2$ C, 40.2; H, 7.39; N, 9.39; S, 21.4%). Found: C, 40.5; H, 7.42; N, 9.41; S, 20.9.

Table II gives the yields and properties of other aminosulfenates prepared this way.

The Reaction of O-Methyl Morpholinosulfenate with Trimethylchlorosilane

The chlorosilane (3.6 g., 1 mol) was added dropwise to the amino sulfenate (5.0 g., 1 mol) with cooling. A yellow mixture resulted which on fractionation gave methoxytrimethylsilane (2.7 g, 78%), bp 57°, n_D^{24} 1.3675 and morpholinosulfenyl chloride (4.8 g, 94%), bp 60°/0.8 mm, n_D^{24} 1.5494.

The Reaction of Diethylamine with O-Methyl Diethylaminosulfenate

The sulfenate (4.7 g, 1 mol) was added to the amine (2.1 g, <1 mol) and the mixture heated for 2 hr. After cooling, the volatile components were pumped off, trapped and redistilled giving methanol (0.4 g), bp 64°, n_D^{17} 1.3311. Excess diethylamine (5.0 g) was heated with the residue and subsequent vacuum distillation gave bis(diethylamino)sulfide (5.0 g, 82%), bp 45°/3 mm, n_D^{18} 1.4622.

The Reaction of O-n-Propyl Dimethylaminosulfenate and Ethanethiol

Excess thiol (2.2 g) was added to the sulfenate (1.1 g) and warmed. The mixture went bright red and after 3 hr., vacuum distillation yielded diethyldisulfide (1.1 g.), bp 35°/12 mm., n_D^{22} 1.5061. The ^{1}H-nmr spectrum showed a quartet centred at 7.33 τ and a triplet at 8.69 τ. A residual distillate on the column was shown by its ^{1}H-nmr spectrum (7.14 τ 4H and 8.62 τ 3H) to be diethyltrisulfide.

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TABLE II
Aminosulfenates Me_2NSOR (R = Me, Et, Pr^n, Bu^n) and R'_2NSOMe (R' = Et, Pr^n)

				Analysis—Found (Calc)			
R(R')	Yield (%)	Bp °C/press. mm	n_d^t	C	H	N	S
Me	85	35/32	1.4390^{24}	33.8 (33.6)	8.13 (8.41)	13.1 (13.1)	29.4 (29.9)
Et	80	32/20	1.4409^{18}	39.3 (39.6)	9.05 (9.14)	10.84 (11.55)	26.9 (26.4)
Pr^n	86	32/3.5	1.4440^{17}	43.7 (44.4)	9.26 (9.68)	10.31 (10.36)	22.8 (23.7)
Bu^n	88	46/4	1.4445^{23}	48.1 (48.3)	9.89 (10.13)	9.88 (9.39)	20.7 (21.5)
(Et)	65	30/4.5	1.4479^{21}	44.5 (44.4)	9.41 (9.62)	10.52 (10.37)	23.3 (23.7)
(Pr^n)	92	36/1	1.4490^{24}	51.2 (51.5)	10.53 (10.43)	9.03 (8.58)	19.9 (19.6)

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