Iminosulfonium Salts and Iminosulfuranes from Thioethers, *N*-Chlorosuccinimide or *N*-Chlorobenzotriazole and Nitrogen-Containing Nucleophiles[1]

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A series of new *N*-alkyl-*S,S*-dimethyliminosulfonium and *N*-aralkyl-*S,S*-dimethyliminosulfonium salts (chlorides and picrates) has been prepared and characterized from alkyl- and aralkylamines, respectively, and dimethyl sulfide "activated" by *N*-chlorosuccinimide or *N*-chlorobenzotriazole. *N*-Chlorosuccinimide and *N*-chlorobenzotriazole have also been shown to be useful thioether "activators" for the preparation of *N*-aryliminosulfuranes, *N*-arylsulfonyliminosulfuranes, and *N*-acyliminosulfonium (and other) salts.

Although many types of N-substituted *S,S*-dialkyliminosulfonium salts and iminosulfuranes (sulfilimines) have been reported during the past decade, virtually no literature exists on the preparation and characterization of *N*-alkyl-*S,S*-dialkyliminosulfonium salts (1), $[R_2S^+NHR]\ A^-$.[2-5] Of the numerous methods available for preparing iminosulfonium salts and iminosulfuranes, the most important and general ones utilize sulfoxides or thioethers as starting materials. Sulfoxides[1b,6] and thioethers[7] are usually "activated" by certain electrophilic species at low temperatures followed by reaction with a nucleophilic nitrogen compound of low basicity. "Activation" consists in providing a leaving group attached to sulfur that can be readily displaced by nucleophiles at low temperatures (Scheme I).

In our earlier studies on the preparation of iminosulfonium salts and iminosulfuranes,[1b,6,7] we were unable to utilize primary aliphatic or aralkylamines successfully as the displacing nucleophiles with "activated" sulfoxides or thioethers. These amines, presumably as a result of their high basicity, are converted to salts, usually hydrochlorides, whereas the less basic arylamines, sulfonamides, and carboxamides effectively perform the nucleophilic displacement shown in Scheme I even though they are weak nucleophiles.

Almost simultaneously in 1972, Johnson, Bacon, and Kingsbury[5] and Vilsmaier and Sprügel[3] reported the reaction of *N*-chlorobenzotriazole (NCB) and *N*-chlorosuccinimide (NCS), respectively, with thioethers followed by reaction with amines to obtain N-substituted *S,S*-dialkyliminosulfonium salts. Although various amines were studied, cyclohexylamine[5] and benzylamine[3] were the only examples reported of the successful use of a primary aliphatic or aralkylamine for the preparation of 1 from "activated" thioethers.[8] In this paper we are reporting (a) the scope and limitations of the use of thioethers "activated" by NCB or NCS for the preparation of 1 and (b) an examination of the generality of NCB or NCS in the preparation of both known and previously unreported iminosulfuranes and iminosulfonium salts from arylamines, sulfonamides, or carboxamides and thioethers.[9]

Results and Discussion

Table I lists *N*-alkyl- and *N*-aralkyl-*S,S*-dimethylsulfonium salts (2–14) prepared (19–97% yields) either from NCS/dimethyl sulfide or NCB/dimethyl sulfide intermediates and alkyl- and aralkylamines. All salts were initially obtained as chlorides but in several cases it was necessary to convert them to picrates to reduce hygroscopicity and increase stability. Except in the cases of unstable compounds, correct elemental analyses were obtained (±0.3%).

With unstable and/or hygroscopic salts that could not be submitted for elemental analysis, NMR and IR spectra were run promptly; spectra were consistent with the proposed structures,[6,7] as was also the case with the compounds that analyzed correctly. Chlorides are water-soluble, white, crystalline solids; picrates are yellow, crystalline solids. Aqueous solutions of chlorides give an immediate precipitate with aqueous silver nitrate. All compounds listed in Table I are new with the exception of the *N*-benzylamine derivative. That compound was first reported by Vilsmaier and Sprügel[3] utilizing the NCS/dimethyl sulfide route but no spectral or analytical data were given. Their published melting point (71–72 °C) does not agree with ours (104–107 °C); they may not have been aware that the chloride is not only hygroscopic but is also difficult to separate from contaminating succinimide (see below).

The NMR spectra of the *N*-alkyl-*S,S*-dimethyliminosulfonium salts (1) clearly show that sulfur bears a high degree of positive charge which significantly deshields the *S*-methyl protons, thereby shifting the signals downfield to δ 3.0–3.4. This downfield shift of *S*-methyl protons is characteristic of iminosulfonium salts and iminosulfuranes.[6,7]

Scheme I

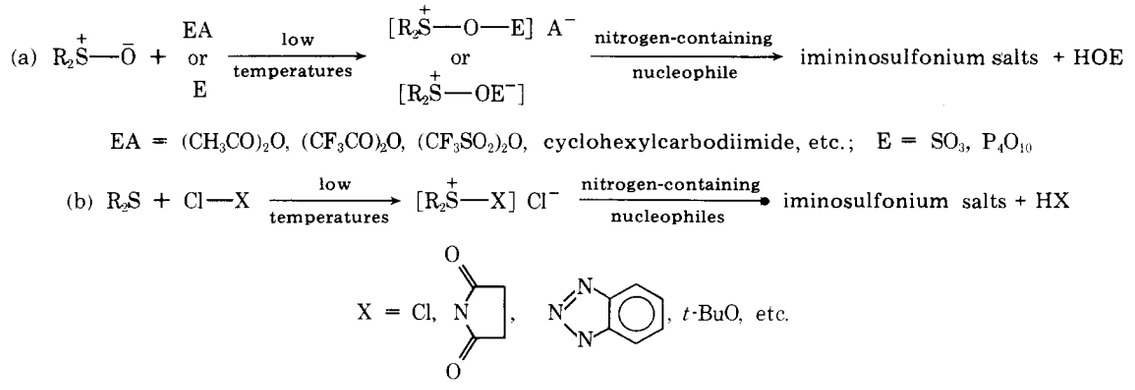
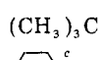
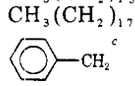
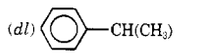
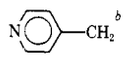


Table I. *N*-Alkyl and -Aralkyl-*S,S*-dimethyliminosulfonium Salts (1), $(CH_3)_2S^+NHR\ A^-$

Registry no.	R	(Compd)	A^-[a]	Yield, %	Mp (dec), °C	Remarks
60978-55-4	CH_3[b]	(2)	C	96	59–63	Hygroscopic; not analyzed
60978-57-6			P		185–190	Unstable; not analyzed
60978-86-1	CH_3CH_2[b]	(3)	C	85		Hygroscopic; not analyzed
60978-59-8			P	19	90–92	[d]
60978-60-1	$(CH_3)_2CH$[b]	(4)	C	63	55–58	Hygroscopic; not analyzed
60978-61-2			P		142–143	[d]
	$CH_3(CH_2)_3$[c]	(5)	C		Oil	Not analyzed
			P	42	Ill-defined	Not analyzed
60978-62-3	$(CH_3)_3C$[b]	(6)	C	58	164.5–165.5	[d]
60978-63-4	 [c]	(7)	C	78	150	[d]
60978-64-5	$(CH_3)_3C(CH_2)_4$[b]	(8)	C	80	108–110	[d]
60978-65-6	1-Adamantyl[c]	(9)	C	85	157.5–158.5	Hygroscopic; not analyzed
60978-67-8			P		188–189	[d]
60978-68-9	$CH_3(CH_2)_{15}$[b]	(10)	C	69	60	[d]
60978-69-0	$CH_3(CH_2)_{17}$[b]	(11)	C	66	70	[d]
35357-68-7	 [c]	(12)	C	80	104–107[e]	Hygroscopic; not analyzed
60978-71-4			P		112–113	[d]
60978-72-5		(13)	C	90+	168–169	[d]
60978-73-6	 [b]	(14)	C	83	95–96	Hygroscopic; unstable above −20 °C
60978-75-8			P		85–90	Unstable; not analyzed

[a] A^-: C = chloride; P = picrate. [b] NCB/$(CH_3)_2S$ used. [c] NCS/$(CH_3)_2S$ used. [d] Correct elemental analysis (±0.3%: C, H, N, S). [e] Lit[3] 71–72 °C. This compound is not stable.

In the preparation of 1 from thioethers and NCS or NCB, succinimide or benzotriazole is produced in equimolar quantities, respectively. This presented a separation problem with succinimide, whose solubility in many organic solvents parallels that of the desired salts. That difficulty could be overcome with stable chlorides by selectively extracting succinimide with ether from 1 in a Soxhlet extractor overnight. This separation procedure is fairly mild and protects hygroscopic salts from atmospheric moisture during workup. With unstable salts, however, the lengthy separation procedure is deleterious. In contrast, benzotriazole is usually easy to separate from 1 by fractional crystallization; thus, NCB is the reactant of choice in most cases. Although NCB is reported to be unstable, we have stored the pure compound in a refrigerator for many months without any detectable deterioration.

To explore the scope of the synthetic utility of NCS/thioether or NCB/thioether intermediates, a series of *N*-aryl-*S,S*-dimethyliminosulfuranes was prepared. Table II lists the compounds prepared (**15–19**) along with yields, melting points, and a comparison of the yields in appropriate cases with those obtained by our previously published Me_2SO/SO_3 procedure.[6] Table II also includes several *N*-aryl-*S,S*-dimethyliminosulfonium salts obtained (**20–23**) during the course of the study.

The NCS and NCB "activation" methods are clearly effective and useful in preparing *N*-aryliminosulfuranes and their salts. The aryl groups may contain electron-withdrawing or -donating substituents. In most cases yields are comparable with those obtained with Me_2SO/SO_3. The NCS/thioether and NCB/thioether procedures, however, require low temperatures whereas the Me_2SO/SO_3 procedure is operative at room temperature or only slightly below.

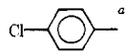
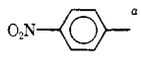
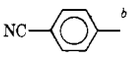
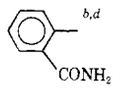
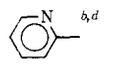
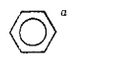
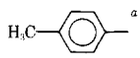
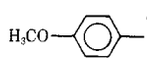
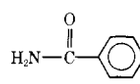
No reaction was obtained between 2,4,6-trichloroaniline or *o*-nitroaniline and the NCS/dimethyl sulfide intermediate; over 80% of the arylamines were recovered. Failure to obtain reaction is attributed to steric hindrance as *p*-nitroaniline reacts and we had shown earlier that bulky ortho substituents interfere with attack of nitrogen nucleophiles on an electrophilic sulfur atom.[6] In the preparation of the *N*-aryliminosulfuranes listed in Table II we have used aqueous base to remove the proton from nitrogen and simultaneously solubilize the by-product succinimide or benzotriazole.

Arylsulfonamides and carboxamides are compounds of low nucleophilicity (relative to arylamines); yet they react readily with the NCB/thioether intermediate. Sulfonamides (*p*-tolyl, phenyl, *p*-chlorophenyl) give generally good yields (40–90%) of *N*-arylsulfonyl-*S,S*-dimethyliminosulfuranes (Table III). Carboxamides (acetamide, benzamide) give only fair yields (40–45%) of *N*-acyl-*S,S*-dimethyliminosulfonium salts (Table IV). Acrylamide was recovered unchanged.

We did not explicitly study the relationship between nucleophilicity of amino (or amido) compound and rate of reaction with the NCB or NCS/thioether intermediate but we anticipated that amines would react more rapidly than amides.[1b] Evidence for different reaction rates was obtained by a study of the reaction of equimolar quantities of *o*-aminobenzamide (anthranilamide) with NCB/$(CH_3)_2S$. This reaction was carried out in a special all-glass apparatus[1b] which permitted formation of the reactive intermediate in one flask and then slow transfer of the intermediate at low temperature with stirring to another flask below it containing the anthranilamide, thereby avoiding an excess of reactive intermediate. The resultant iminosulfurane (**18**) was formed exclusively on the amino function, as expected (spectral characterization), although the yield was only fair.

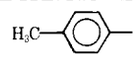
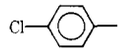
Thioethers other than dimethyl sulfide can also be used. With α-methylbenzylamine (*dl*, *l*, or *d*) as the model amine, we obtained excellent yields (40–96%) of iminosulfonium chlorides from NCS-"activated" diethyl sulfide and tetramethylene sulfide, as well as from dimethyl sulfide (Table V). Di-*tert*-butyl sulfide, diphenyl sulfide, and thiophene did not react with aniline, benzylamine, or α-methylbenzylamine, three amines that react satisfactorily with "activated" dimethyl sulfide. The amine (hydrochloride) was recovered. NCS-"activated" di-(*p*-methoxyphenyl) sulfide, bis(β-chlo-

Table II. *N*-Aryl-*S*,*S*-dimethyliminosulfuranes $(CH_3)_2S^+N^-R$, and *N*-Aryl-*S*,*S*-dimethyliminosulfonium Salts, $(CH_3)_2S^+NHR\ Cl^-$

Registry no.	R	(Compd)	Yield, %	Mp, °C	Me_2SO/SO_3 method[6] Yield, %	Me_2SO/SO_3 method[6] Mp, °C
		Iminosulfuranes				
60978-76-9		(15)	66	63–64	75	66.5–67.5
31896-57-8		(16)	80	162–163	90	168–170
60978-77-0		(17)	77	107–108	62	111–112
60978-78-1		(18)	25	120–131	*c*	*c*
60978-79-2		(19)	41	83–84	*c*	*c*
		Iminosulfonium Salts				
35357-64-3		(20)	85	110 dec (104–105)[3]	*c*	*c*
60978-80-5		(21)	67	111–112 dec	*c*	*c*
35357-66-5		(22)	68	128–130 dec (115–116)[3]	*c*	*c*
60978-81-6		(23)	43	152–153 dec	*c*	*c*

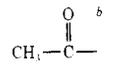
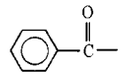
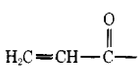
[a] $NCS/(CH_3)_2S$ used. [b] $NCB/(CH_3)_2S$ used. [c] Not studied. [d] Correct elemental analysis.

Table III. *N*-Arylsulfonyl-*S*,*S*-dimethyliminosulfuranes,[a] $(CH_3)_2S^+N^-SO_2R$

Registry no.	R	(Compd)	Yield, %	Mp, °C	Me_2SO/SO_3 method[6] Yield, %	Me_2SO/SO_3 method[6] Mp, °C
31657-41-7		(24)	89	156–158	80	156–158
60978-82-7		(25)	37	129–130	75	131
60978-83-8		(26)	70	113–115	91	122–123

[a] $NCB/(CH_3)_2S$ used.

Table IV. *N*-Acyl-*S*,*S*-dimethyliminosulfonium Salts,[a] $(CH_3)_2S^+NHR\ Cl^-$

R	(Compd)	Yield, %	Mp, °C	Lit. mp, °C
	(27)	45	124	131–133[3,11]
	(28)	42	105	108–109[12,16]
	No reaction			

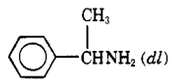
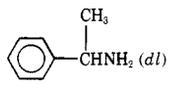
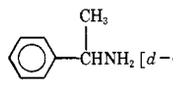
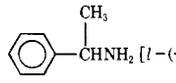
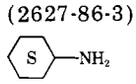
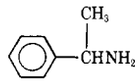
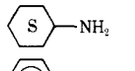
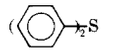
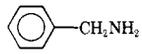
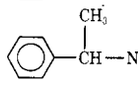
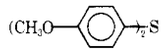
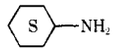
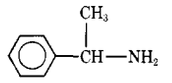
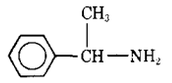
[a] $NCB/(CH_3)_2S$ used. [b] The acetamide–chloroform solution used in this preparation must be carefully dried.

roethyl) sulfide, and bis(β-cyanoethyl) sulfide yielded unstable products that decomposed in a complex way on reaction with cyclohexylamine and α-methylbenzylamine (Table V).

Failure of di-*tert*-butyl sulfide to react was anticipated as we had observed such behavior before.[7,13] Earlier findings of Kingsbury and Johnson[14] had shown that di-*tert*-butyl sulfide is not converted to sulfoxide by NCB in methanol. We attribute failure to react a result of steric hindrance to attack on the bulky thioether by the large activating species (NCB). Failure of diphenyl sulfide or thiophene to react is attributed to reduction in nucleophilicity of the sulfur atom by the aromatic ring(s). To overcome the effect of reduced electron density on sulfur in aromatic thioethers we prepared di(*p*-methoxyphenyl) sulfide. This thioether seemed to form an "activated" intermediate and yielded an iminosulfonium salt when treated with cyclohexylamine but the resulting product was quite unstable.

Comparison of the NCB or NCS/thioether procedure with numerous literature methods for preparing iminosulfuranes shows that this procedure is equal to or superior to previously described methods.[1b,6,10] In addition, the NCB and NCS procedures now make readily available a variety of *N*-alkyl-

Table V. Miscellaneous *S,S*-Dialkyliminosulfonium Chlorides[a]

Thioether	Amine	Iminosulfonium chloride Yield, %	(Compd)	Mp, °C
$(C_2H_5)_2S$		44	(29)	110
(352-93-2)[d]	(618-36-0)[d]		(60978-84-9)[d]	
		95	(30)	174–175 dec
(110-01-0)			(60978-85-0)	
		95	(31)	172–173 dec
	(3886-69-9)		(61045-15-6)	
		95	(32)	172–173 dec
	(2627-86-3)		(61045-16-7)	
$(CH_3)_2S$[b]		78	(7)	150
$(CH_3)_2S$[b,c]		90+	(13)	168–169 dec
$[(CH_3)_3C]_2S$		No reaction		
		No reaction		
		No reaction		
		Decomposition		
$(ClCH_2CH_2)_2S$		Decomposition		
$(CNCH_2CH_2)_2S$		Decomposition		

[a] NCS/thioether "activation," except where indicated. [b] See Table I. Listed here for comparison purposes. [c] NCB "activation." [d] Registry no.

and -aralkyliminosulfonium salts, compounds difficult, if not impossible, to obtain by older methods.

Experimental Section[15]

***N*-Alkyl-*S,S*-dimethyliminosulfonium Salts (Table I). A. *N*-Cyclohexyl-*S,S*-dimethyliminosulfonium Chloride (7).** Dimethyl sulfide (2.0 ml, 27.5 mmol, 10% excess) was dissolved in CH_2Cl_2 (75 ml) and cooled to −50 to −60 °C in a 250-ml, three-neck flask fitted with a stirrer, dropping funnel, thermometer, and drying tube. NCS (3.38 g, 25 mmol) dissolved in CH_2Cl_2 (50 ml) was added dropwise; a dense white precipitate formed. Stirring was continued for 1 h below −40 °C followed by the dropwise addition of cyclohexylamine (3.05 ml, 25 mmol) dissolved in CH_2Cl_2 (10 ml). After an additional 1 h of stirring below −40 °C, the reaction mixture was allowed to warm to room temperature and all volatiles were then removed in a rotary evaporator. The residue was transferred to the cup of a Soxhlet extractor and extracted overnight with ether. The white, insoluble solid residue (3.75 g, 78%) of crude **7**, mp 141–142 °C dec, was recrystallized to constant melting point from CH_2Cl_2/ether: mp 150 °C dec (single TLC spot); NMR ($CDCl_3$) cyclohexyl H (δ 1.0–2.2, broad s, 11 H); $^+S(CH_3)_2$ (3.42, s, 6 H); NH (7.92, d, 1 H). The NH signal disappeared upon addition of D_2O. Anal. Calcd for $C_8H_{18}ClNS$: C, 49.1; H, 9.27; N, 7.16; S, 16.4. Found: C, 49.2; H, 9.08; N, 7.19; S, 16.2.

B. *N*-*tert*-Octyl-*S,S*-dimethyliminosulfonium chloride (8) was prepared from dimethyl sulfide (2.0 ml, 27.5 mmol), NCB (3.84 g, 25 mmol), *tert*-octylamine (3.23 g, 25 mmol), and CH_2Cl_2 (170 ml) except that the reaction solution was not evaporated to dryness but to a volume of about 100 ml, followed by addition of ether to the cloud point. Storage of the mixture overnight at −20 °C yielded a precipitate of crude **8** (5.0 g, 90%), mp 102–104 °C dec, which was recrystallized to constant melting point from CH_2Cl_2/ether: mp 108–110 °C dec (single TLC spot); NMR ($CDCl_3$) $C(CH_3)_3$ (δ 0.85, s, 9 H), CH_2 (1.37, m, 8 H), $^+S(CH_3)_2$ (3.44, s, 6 H), NH (7.97 broad s, 1 H). Anal. Calcd for $C_{10}H_{24}ClNS$: C, 53.2; H, 10.7; N, 6.20; S, 14.2. Found: C, 53.4; H, 10.8; N, 6.19; S, 13.9.

C. *N*-Benzyl-*S,S*-dimethyliminosulfonium chloride and picrate (12) were prepared as in A from dimethyl sulfide, NCS, benzylamine, and CH_2Cl_2 (160 ml). The crude chloride (4.62 g, 80%), mp 100–102 °C dec, remaining in the Soxhlet cup was recrystallized to constant melting point from CH_2Cl_2/ether: mp 104–107 °C dec (single TLC spot) (lit.[3] 71–72 °C; see Table I and text); NMR ($CDCl_3$) $^+S(CH_3)_2$ (δ 3.14, s, 6 H), CH_2 (4.14, d, 2 H), aromatic H (7.26, broad s, 5 H), NH (8.48, broad s, 1 H) (the NH signal disappeared on addition of D_2O); IR (KBr) 2780 and 700 cm^{-1} (strong).

As the chloride is hygroscopic, a portion was converted to the picrate by treatment of an aqueous solution with saturated aqueous picric acid. The yellow crstals that formed on cooling were recrystallized from absolute ethanol, mp 112–113 °C dec. Anal. Calcd for $C_{15}H_{16}N_4O_7S$: C, 45.5; H, 4.07; N, 14.1; S, 8.09. Found: C, 45.8; H, 4.09; N, 14.1; S, 7.86.

D. Miscellaneous Preparative Details. With the exceptions noted in Table I (**6, 7, 8, 10, 11, 13**), chlorides were too hygroscopic or unstable to be submitted for analysis. Picrates were less hygroscopic and more stable, and satisfactory analyses could be obtained in some cases (**3, 4, 9, 12**). Compounds **2, 5,** and **14,** as chlorides or picrates, were not analyzed but their NMR spectra were consistent with the

proposed structures. Picrates were usually prepared from methanol or ethanol solutions of the chlorides and an excess of a saturated solution of picric acid in the same solvent. Chlorides (**10, 11**) prepared from hexadecyl- and octadecylamines were waxy solids of somewhat ill-defined melting points. They appeared to be stable and relatively nonhygroscopic but they (as well as other stable chlorides) were stored in a desiccator over a drying agent as a routine precaution. Aqueous solutions of chlorides gave an immediate precipitate on addition of silver nitrate solution.

***N*-Aryliminosulfuranes and *N*-Aryliminosulfonium Chlorides (Table II). A. *N*-*p*-Chlorophenyl-*S,S*-dimethyliminosulfurane (15).** **15** was prepared from dimethyl sulfide, NCS, *p*-chloroaniline, and CH_2Cl_2 (200 ml) except that excess aqueous NaOH (50 ml of 1 N) was added to the reaction mixture after it had reached room temperature. The CH_2Cl_2 solution was separated, washed with water (50 ml), dried ($MgSO_4$), and evaporated to dryness in a rotary evaporator. The residue (6.0 g), a yellow oil, showed only two spots on TLC examination, R_f 0.28 (identical with authentic **15**)[6] and 0.65 (succinimide). Crystallization from ether/hexane yielded pure **15** (3.1 g, 68%), mp 63–64 °C (lit.[6] 66–67 °C) (NMR and IR identical with those of an authentic sample).

B. *N*-*p*-Nitrophenyl-*S,S*-dimethyliminosulfurane (16) was similarly prepared using *p*-nitroaniline instead of *p*-chloroaniline and acetonitrile/CH_2Cl_2 (1:1) instead of CH_2Cl_2 to assist the dissolution of the amine at low temperatures. Crude **16** (3.96 g, 80%), mp 156–158 °C, was crystallized from ethyl acetate/pentane, mp 162–163 °C (lit.[6] 168–170 °C) (NMR and IR identical with those of an authentic sample).

C. *N*-*p*-Cyanophenyl-*S,S*-dimethyliminosulfurane (17) was prepared from dimethyl sulfide, NCB, *p*-cyanoaniline, and CH_2Cl_2 (180 ml). Crude **17** (4.8 g) was crystallized from CH_2Cl_2/ether, mp 107–108 °C (lit.[6] 111–112 °C) (3.4 g, 77%) (NMR and IR identical with those of an authentic sample).

D. *N*-2-Pyridino-*S,S*-dimethyliminosulfurane (19) was prepared from dimethyl sulfide, NCB, 2-aminopyridine, and CH_2Cl_2 (140 ml). Crude **19** was dissolved in chloroform (100 ml) and washed with dilute aqueous NaOH and then with water to remove benzotriazole contaminant. The chloroform solution was dried ($MgSO_4$), ether was added to the cloud point, and the mixture was cooled overnight at −20 °C. Pure **19**, mp 83–84 °C, was isolated by filtration (1.58 g, 41%): NMR ($CDCl_3$) $^+S(CH_3)_2$ (δ 2.66, s, 6 H), aromatic H (7.22–7.92, m, 4 H). Anal. Calcd for $C_7H_{10}N_2S$: C, 54.5; H, 6.53; N, 18.2. Found: C, 54.5; H, 6.58; N, 17 9.

E. *N*-*o*-Carboxamidophenyl-*S,S*-dimethyliminosulfurane (18) was prepared using the "inverse addition" technique and dual reaction flask apparatus previously reported by us.[1b] Dimethyl sulfide (2.0 ml, 27.5 mmol) was dissolved in acetone (25 ml) in the upper flask and the solution was cooled to −50 to −60 °C with stirring followed by dropwise addition of NCB (3.84 g, 25 mmol), dissolved in acetone (30 ml). A dense white precipitate formed and stirring was continued for 1 h below −40 °C. The slurry was then added slowly with stirring to the lower flask which contained *o*-aminobenzamide (3.4 g, 25 mmol) dissolved in acetone (100 ml) and cooled to −50 to −60 °C. After 1 h, triethylamine (3.5 ml, 25 mmol) dissolved in acetone (20 ml) was added and the reaction mixture was then allowed to warm to room temperature. Triethylamine hydrochloride was filtered off and the filtrate was evaporated to dryness in a rotary evaporator yielding crude **18** as a light tan solid (mp 108–110 °C). It was dissolved in CH_2Cl_2 and treated with activated carbon, and ether was added to the cloud point. Cooling to 0 °C yielded analytically pure **18**: mp 130–131 °C (1.2 g, 25% yield) [single spot on TLC, R_f 0.375 (silica gel/acetone)]; NMR (D_2O) $^+S(CH_3)_2$ (δ 2.68, s, 6 H), aromatic H (6.76–8.16, m, 4 H); IR (KBr) 753, 792, 921, 1162, 1222, 1262, 1480, 1640, 3250 cm^{-1}. The position of the C=O absorption was the same as that in *o*-aminobenzamide, thus demonstrating that ylide formation had *not* occurred on the carboxamido group. Anal. Calcd for $C_9H_{12}N_2OS$: C, 55.1; H, 6.16; N, 14.3; S, 16.3. Found: C, 55.1; H, 6.14; N, 14.1; S, 16.5.

F. *N*-Phenyl-*S,S*-dimethyliminosulfonium chloride (20) was prepared from dimethyl sulfide, NCS, aniline, and CH_2Cl_2 (135 ml). Extraction of crude **20** with ether in a Soxhlet extractor yielded **20** (4.03 g, 85%), mp 110 °C dec, a hygroscopic, somewhat unstable compound that did not yield an insoluble picrate: NMR ($CDCl_3$) $^+S(CH_3)_2$ (δ 3.38, s, 6 H), aromatic H (7.22, broad s, 5 H).

G. *N*-*p*-Tosyl-*S,S*-dimethyliminosulfonium chloride (21) and *N*-*p*-methoxyphenyl-*S,S*-dimethyliminosulfonium chloride (22) were prepared in the same way as **20** except for the use of *p*-toluidine and *p*-anisidine, respectively. Both salts are unstable. NMR: compound **21** ($CDCl_3$/Me_2SO-d_6), $ArCH_3$ (δ 2.34, s), $^+S(CH_3)_2$ (3.44, s), aromatic H (7.14, 7.44, dd); compound **22** (Me_2SO-d_6), $^+S(CH_3)_2$ (δ 3.48, s, 6 H), CH_3O (3.76, s, 3 H), aromatic H (6.84, 7.10, dd, 4 H), NH (9.89, broad s, 1 H).

H. *N*-*p*-Carboxamidophenyl-*S,S*-dimethyliminosulfonium chloride (23) was prepared from dimethyl sulfide, NCB, *p*-aminobenzamide (125 ml of acetonitrile was used to dissolve the amide), and CH_2Cl_2 (100 ml): NMR (D_2O) $^+S(CH_3)_2$ (3.39, s, 6 H), aromatic H (7.24, 7.84, dd, 4 H).

***N*-Arylsulfonyl-*S,S*-dimethyliminosulfuranes (24–26) (Table III). *N*-*p*-Toluenesulfonyl-*S,S*-dimethyliminosulfurane (24)** was prepared from dimethyl sulfide, NCB, and CH_2Cl_2 (125 ml); *p*-toluenesulfonamide (25 mmol) dissolved in acetone (50 ml) was added to the CH_2Cl_2 solution of the "activated" thioether. After 1 h at −40 °C, the reaction mixture was allowed to warm to room temperature and aqueous NaOH (50 ml, 25 mmol) was added. Crude **24** isolated by evaporation was dissolved in CH_2Cl_2, ether was added to the cloud point, and the mixture was cooled overnight to −20 °C. Pure **24** was isolated by filtration (5.12 g, 89%), mp 156–158 °C (lit.[6] 156–158 °C), identical in every respect with an authentic specimen.

Compounds **25** (*N*-benzenesulfonyl-) and **26** (*N*-*p*-chlorophenylsulfonyl-) were similarly prepared in 37 and 70% yields, respectively, except that benzenesulfonamide was added in 1:1 acetone/CH_2Cl_2 (50 ml) and *p*-chlorobenzenesulfonamide was added in CH_2Cl_2 solution (50 ml).

***N*-Acyliminosulfonium Salts (27 and 28) (Table IV). *N*-Acetyl-*S,S*-dimethyliminosulfonium chloride (27)** was prepared from dimethyl sulfide, NCB, and acetamide in chloroform (50 ml; solution carefully dried) and CH_2Cl_2 (100 ml). After reaching room temperature, the reaction mixture was concentrated under vacuum to ca. 100 ml followed by addition of ether to the cloud point. The mixture was cooled to −20 °C and crystalline **27** (hygroscopic) was isolated by filtration (1.75 g, 45%), mp 124 °C (lit.[3,11] 131 °C). The NMR and IR spectra were virtually identical with those of an authentic specimen of the corresponding bromide[11] and confirmed the structure.

The *N*-benzoyl analogue (**28**) was similarly prepared except that benzamide was added in CH_2Cl_2 (50 ml) and the crude product was extracted overnight with ether in a Soxhlet extractor. The insoluble residue consisted of pure **28** (2.3 g, 42%), mp 105 °C (lit.[12,16] 108 °C). NMR and IR were consistent with the structure.

Miscellaneous Iminosulfonium Chlorides (Table V). A. *N*-(*dl*)-α-Methylbenzyl-*S,S*-diethyliminosulfonium chloride (29) was prepared from diethyl sulfide (2.97 ml, 27.5 mmol, 10% excess) in CH_2Cl_2 (75 ml) cooled to −50 °C to which NCS (3.34 g, 25 mmol) was added (a dense white precipitate formed) followed after 1 h by (*dl*)-α-methylbenzylamine (3.23 ml, 25 mmol), dissolved in CH_2Cl_2 (20 ml). After an additional 1 h below −40 °C, the reaction mixture was allowed to warm to room temperature and the solvent was evaporated in a rotary evaporator. The residual oil was dissolved in acetone and ether was added to the cloud point. The mixture was cooled overnight at −20 °C and the white, crystalline product (**29**) was collected by filtration (2.7 g, 44%), mp 110 °C. The product was hygroscopic but stable: NMR ($CDCl_3$) CH_3CH_2 (δ 1.20, 1.44, t, t, 6 H), CCH_3 (1.68, d, 3 H), CH_3CH_2 (3.52, 3.90, m, m, 4 H); CH (4.16, m, 1 H); aromatic H (7.40, broad s, 5 H), NH (8.52, broad s, 1 H). Anal. Calcd for $C_{12}H_{20}ClNS$: C, 58.7; H, 8.20; N, 5.70; S, 13.1. Found: C, 58.8; H, 8.13; N, 5.69; S, 13.2.

B. *N*-(*dl*)-α-Methylbenzyl-*S,S*-tetramethyleneiminosulfonium chloride (30) was prepared as described in A but substituting tetramethylene sulfide for diethyl sulfide and extracting the crude solid residue with ether in a Soxhlet extractor overnight. Crude residual **30** (4.96 g, 95%), mp 161–163 °C, was recrystallized from CH_2Cl_2/ether to yield the analytically pure salt, mp 174–175 °C. Its NMR spectrum ($CDCl_3$), although complex, could be readily interpreted and the integrated values for all of the protons were correct. The signal for the NH proton disappeared upon addition of D_2O. Anal. Calcd for $C_{12}H_{18}ClNs$: C, 59.1; H, 7.44; N, 5.75; S, 13.2 Found: C, 59.3; H, 7.33; N, 5.86; S 13.4.

Compounds **31**, mp 172–173 °C dec, and **32**, mp 172–173 °C dec, were prepared in the same way in over 95% yields utilizing the enantiomeric (*d*)- and (*l*)-α-methylbenzylamines. The specific rotations were $[+0.43°]^{25}_{D,CH_3OH}$ and $[-0.47°]^{25}_{D,CHOH}$, respectively. Their NMR spectra (DCl_3) were virtually identical with that of **30**.

Acknowledgment. This investigation was supported in part by Grants 07803, 05280, and 12227, awarded by the National Cancer Institute, DHEW, and the Samuel S. Fels Fund. One of us (A.D.D.) thanks the Armstrong Cork Co. for a research fellowship.

Registry No.—Dimethyl sulfide, 75-18-3; cyclohexylamine, 108-91-8; *tert*-octylamine, 60996-53-4; benzylamine, 100-46-9; hex-

adecylamine, 143-27-1; octadecylamine, 124-30-1; *p*-chloroaniline, 106-47-8; *p*-nitroaniline, 100-01-6; *p*-cyanoaniline, 873-74-5; 2-aminopyridine, 504-29-0; aniline, 62-53-3; *p*-toluidine, 106-49-0; *p*-anisidine, 104-94-9; *p*-aminobenzamide, 2835-68-9; *p*-toluenesulfonamide, 70-55-3; benzenesulfenamide, 98-10-2; *p*-chlorobenzenesulfonamide, 98-64-6; NCS, 128-09-6; NCB, 128-08-5; methylamine, 74-89-5; ethylamine, 75-04-7; isopropylamine, 75-31-0; butylamine, 109-73-9; *tert*-butylamine, 75-64-9; 1-adamantylamine, 768-94-5; 4-aminomethylpyridine, 3731-53-1; 2-aminobenzamide, 88-68-9.

References and Notes

(1) (a) Parts of this paper have been presented at the 9th Middle Atlantic Regional Meeting of the American Chemical Society, Wilkes-Barre, Pa., April 1974; VIth International Symposium on Sulfur Chemistry, Bangor, Wales, July 1974; and 7th Central Regional Meeting of the American Chemical Society, Morgantown, W.Va., May 1975; taken from the Ph.D. Thesis of A. D. Dawson, Temple University, 1975. (b) This is part 16 in the Iminosulfuranes series. Part 15: A. K. Sharma, T. Ku, A. Dawson, and D. Swern, *J. Org. Chem.*, **40**, 2758 (1975).

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(8) Knoll, Mueller-Kalben, and Appel[2b] prepared three *N*-alkyl-*S*,*S*-dialkyliminosulfonium hexachloroantimonates in good yield from dimethyl (or methyl ethyl) chlorosulfonium hexachloroantimonates and isopropylamine or 1,2-ethylenediamine; melting points, NMR spectra, and elemental analyses were given. Appel and Büchner[2a] mentioned the preparation of *N*-cyanoethyl-*S*,*S*-diethyliminosulfurane (but not its salts) from diethylsulfilimine and acrylonitrile but without supporting details or characterization (W. Büchner, Dissertation, University of Heidelberg, 1960; not available to us). M. Haake and H. Benack, *Synthesis*, 308, 310 (1976), recently reported the preparation of alkyl(aryl)dialkylaminosuccinimidosulfonium salts from sulfenamides and NCS, and have also prepared ylides from the salts.

(9) After our study had been completed, P. Claus, W. Rieder, P. Hofbauer, and E. Vilsmaier, *Tetrahedron*, **31**, 505 (1975), reported the use of NCS for the efficient preparation of *N*-arylsulfilimines (*N*-aryliminosulfuranes) and their picrates from thioethers and arylamines. In the few cases where duplication of compounds exists, their results and ours agree. However, as we had reported earlier,[1a] the NCS and NCB pathways can also be employed with sulfonamides and carboxamides.

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(15) Dimethyl sulfide, diethyl sulfide, diphenyl sulfide, tetramethylene sulfide, and thiophene (Aldrich) were dried with freshly activated (450 °C, 12 h) Linde molecular sieves before use. β,β'-Dicyanodiethyl sulfide (Aldrich) was used as received. Triethylamine (Aldrich) was purified by fractional distillation from phenyl isocyanate. *N*-Chlorosuccinimide (Arapahoe or Aldrich) was recrystallized from hot water. *N*-Chlorobenzotriazole was prepared by the literature procedure.[5] Methylamine and ethylamine (MCB) were condensed from cylinders. Isopropylamine, butylamine, benzylamine, cyclohexylamine, α-methylbenzylamine, *o*- and *p*-nitroaniline, *p*-chloroaniline, *p*-toluenesulfonamide, *p*-chlorobenzenesulfonamide (Eastman), *d*- and *l*-α-methylbenzylamine, adamantylamine, *p*-aminobenzonitrile, *o*-aminobenzamide (Aldrich), *tert*-octylamine (Rohm and Haas), hexadecylamine, octadecylamine (Armour), and benzenesulfonamide (MCB) were used as received; in all cases purity was 97% or greater. All solvents were the purest and driest grades; they were purified when necessary. For IR, a Perkin-Elmer Infracord 137B or Pye Unicam SP 1000 were used. For NMR, a Varian A-60A or XL-100 with tetramethylsilane or 2,2-dimethyl-2-silapentane-5-sulfonate (Norell) as internal standards were used. Melting points (uncorrected) were taken on a Thomas-Hoover capillary apparatus. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del. For TLC, Eastman silica gel Chromagrams or Analtech prescored silica gel plates with fluorescent indicator were used. Spots were visualized under UV or by development in a closed chamber containing iodine crystals.

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Synthesis of 2,4,6-Trinitrobenzenesulfenyl Chloride and Derivatives[1a]

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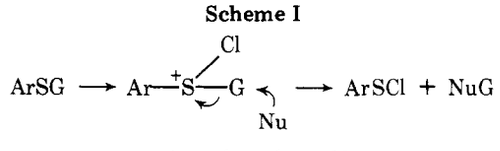
Received August 10, 1976

The synthesis of 2,4,6-trinitrobenzenesulfenyl chloride was accomplished by chlorinolysis of phenyl 2,4,6-trinitrophenyl disulfide which could be prepared by reaction of potassium thiopicrate with benzenesulfenyl chloride. The sulfenyl chloride reacted with alcohols, secondary amines, and the silver salts of N-alkylsulfonamides to afford, respectively, sulfenate esters, sulfenamides, and sulfenylsulfonamides.

Nitrobenzenesulfenyl chlorides are well known and the subjects of an extensive literature.[2] The *o*- and *p*-nitrobenzenesulfenyl chlorides are easily prepared and have received considerable attention. The synthesis of 2,4-dinitrobenzenesulfenyl chloride is the subject of an *Organic Syntheses* preparation[3] and is readily available from commercial sources. It has found application not only in synthetic and analytical chemistry, but also in natural product chemistry as a protecting group for the hydroxyl function and numerous derivatives have been characterized.[4] By contrast, 2,4,6-trinitrobenzenesulfenyl chloride (1) heretofore has been a completely unknown compound. In the course of our investigations of the dynamic stereochemistry of sulfenamides,[5] we became interested in 1 and have directed our efforts to its synthesis and the preparation of some of its derivatives.[6]

The mononitro- and dinitrobenzenesulfenyl chlorides are readily prepared by chlorinolysis of the corresponding thiols, symmetrical disulfides, or sulfides using chlorine gas or sulfuryl chloride as the chlorinating agent.[2,3] All of these reactions presumably involve electrophilic attack at sulfur followed by nucleophilic displacement of the sulfenyl chloride as a neutral leaving group (Scheme I).

Scheme I



This sequence requires that the sulfur atom act as a nucleophile in the initial step leading to the formation of the chlorosulfonium ion and the presence of an additional ortho nitro group suggests that this step should be less favorable for the synthesis of 1 as compared with its mono- and dinitro analogues. In accord with this expectation, Kharasch et al. were unable to prepare 1 by chlorinolysis of benzyl 2,4,6-trinitrophenyl sulfide (2) using sulfuryl chloride, although this