Syntheses of Diaza-, Azaoxa-, Diazaoxa-, and Triazasulfonium Ions

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Methods for synthesizing diaza-, azaoxa-, diazaoxa-, and triazasulfonium tetraphenylborates were described, and some of their reactivities were discussed.

Sulfonium ions substituted by heteroatoms are of considerable interest, and aza-, oxa-, and thiasulfonium ions have been studied to a great extent.[1] Only a few studies, however, have been carried out on diaza-, azaoxa-, diazaoxa-, and triazasulfonium ions. Syntheses of these sulfonium ions have been investigated in our laboratories, and the results are described in this paper.

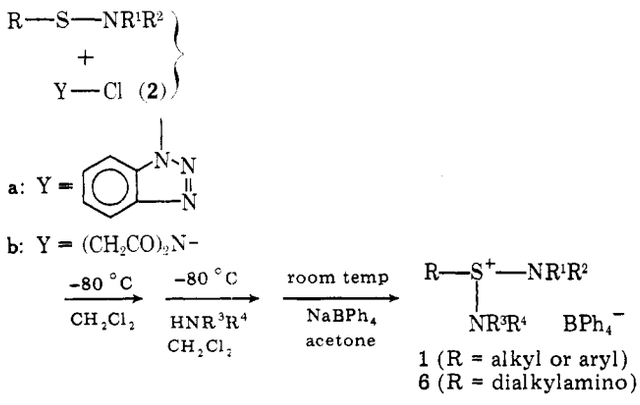
Results and Discussion

Diazasulfonium Ions. Richards and Tarbell prepared ethyldimorpholinosulfonium tetrafluoroborate by the reaction of dimorpholino sulfide and triethyloxonium tetrafluoroborate.[2] They stated, however, that "numerous other alkylation reactions of amine sulfides with a variety of alkylating agents did not yield isolable products". We also examined reactions of various alkylating agents and various diamino sulfides, but none of our attempts yielded diazasulfonium salts. Thus, alkylations of diamino sulfides cannot be a general method for preparing diazasulfonium salts.

Johnson, Bacon, and Kingsbury prepared azasulfonium salts by the treatment of sulfides with 1-chlorobenzotriazole followed by the addition of amines and silver tetrafluoroborate.[3] Vilsmaier and Sprügel synthesized azasulfonium salts from sulfides, *N*-chlorosuccinimide, and amines.[4] In view of these reactions, treatments of sulfenamides with *N*-halo compounds and then with amines were investigated as a possible method for the synthesis of diazasulfonium salts.

It was found that diazasulfonium salts **1a–f** summarized in Table I were successfully prepared by the treatment of an alkane or arene sulfenamide with 1-chlorobenzotriazole (**2a**) or *N*-chlorosuccinimide (**2b**) in dichloromethane followed by the addition of a secondary amine at −80 °C and the addition of sodium tetraphenylborate (**3**) at room temperature.

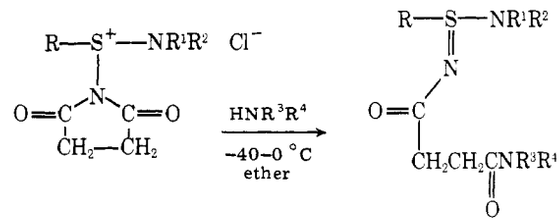
Method A



1 (R = alkyl or aryl)
6 (R = dialkylamino)

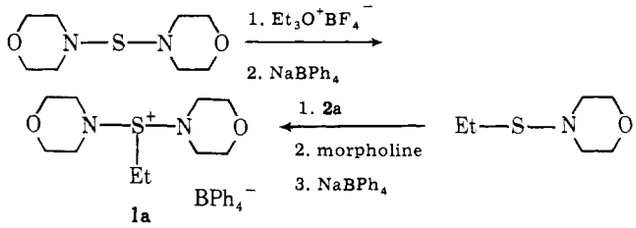
Although both **2a** and **2b** are effective for oxidation of sulfides, yields are higher when **2a** is used (yields of **1b** with **2a**, 65%; with **2b**, 51%).

After our work was completed, Haake and Benack reported in a communication that, when a suspension of an adduct formed from a sulfenamide and **2b** was treated in ether between −40 and 0 °C with 2 equiv of a secondary amine (morpholine or diethylamine), no displacement of succinimide was detected and the succinimide ring was always opened, forming sulfinamidine derivatives in 67–89% yields.[5]



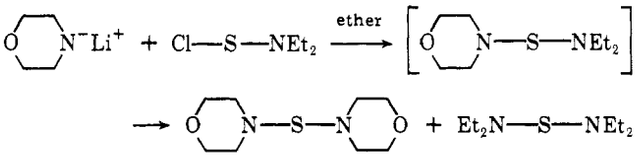
It is of interest that a slight difference in the reaction conditions results in the formation of different product. It is possible that the lower yields of **1** observed by use of **2b** in our system are due to concurrent occurrence of the ring opening, but only the crystalline products were isolated and products of side reactions were not determined.

In order to compare **1a** prepared by method A with the salt prepared by Richards and Tarbell,[2] we treated dimorpholino sulfide with triethyloxonium tetrafluoroborate and exchanged the anion of the salt with BPh_4^-. The ^1H NMR spectra and the melting points showed that these two salts were identical.



When diphenylamine was allowed to react with a mixture of *N*-methanesulfenylpiperidine and **2a** at −80 °C and then **3** was added, the product isolated was a diaminosulfonium ion containing no diphenylamine moiety and was found to be **1c** (25% yield). Apparently, the weakly nucleophilic diphenylamino group cannot react with the intermediate, which decomposed upon warming and yielded **1c**.

When two dialkylamino groups of **1** are different, such sulfonium ions are chiral. If chiral **1** is to be prepared by alkylation of diamino sulfides, one must have diamino sulfides possessing two different amino groups. Harpp and Back[6] attempted to prepare such sulfides from the reaction of a dialkylamino phthalimido sulfide and another dialkylamine, but they obtained two kinds of symmetric diamino sulfides, presumably formed by disproportionation of the expected product. We attempted to prepared diethylamino morpholino sulfide from the reaction of diethylaminosulfenyl chloride and lithium morpholide in ether. However, during the process of



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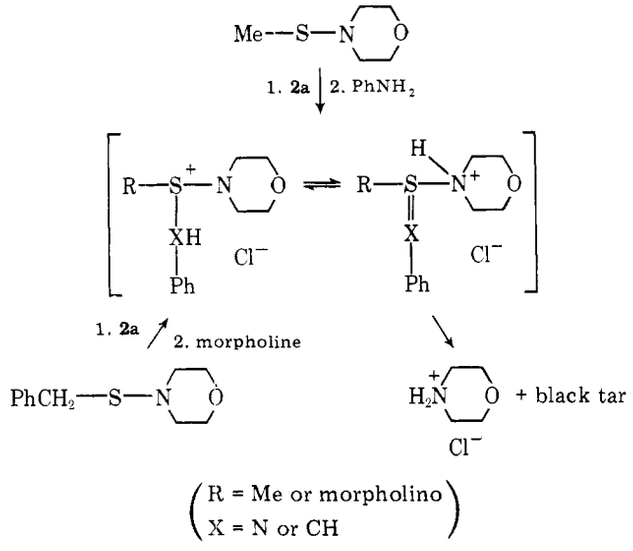
purification, disproportionation proceeded, and it was not possible to isolate the pure sulfide.

However, when one uses method A for the preparation of **1** from sulfenamides, **2**, and secondary amines, diazasulfonium ions possessing two different amino groups (such as **1d–f**) can readily be prepared. By use of optically active anions, it would be possible to resolve them.

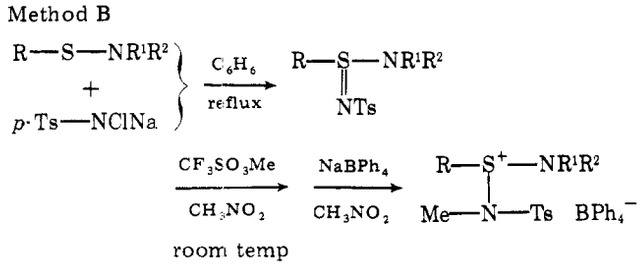
In an attempt to prepare an aminosulfilimine, aniline was added to a mixture of *N*-methanesulfenylmorpholine and **2a** at −80 °C. The color of the solution changed from pale yellow to orange, to deep red, and finally to black, and morpholinium chloride precipitated almost quantitatively. The anilino proton in the anilinomorpholinosulfonium ion appears to be quite labile.

In an attempt to prepare a diazasulfonium ylide, the synthesis of benzyldimorpholinosulfonium ion was investigated. However, as soon as morpholine was added to a mixture of *N*-(phenylmethanesulfenyl)morpholine and **2a** at −80 °C, morpholinium chloride precipitated. The benzyl protons in the benzylmorpholinosulfonium ion formed appears to be quite labile. These results show that diazasulfonium ions tend to decompose when they have labile α protons.



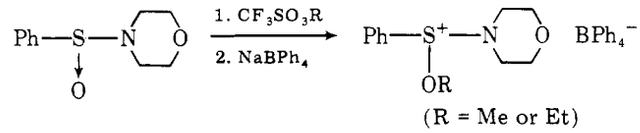
The reactivities of diazasulfonium ions were investigated by allowing an equimolar mixture of **1b**, dimsyl sodium, and benzophenone to react in dimethyl sulfoxide for 1 h at 50 °C. The product formed was *N*-methanesulfenylmorpholine, and no products indicative of the formation of a ylide were found. Richards and Tarbell[2] reported similar results in the reaction of ethyldimorpholinosulfonium tetrafluoroborate with butyllithium. When **1** was mixed with sodium methoxide in methanol at −40 °C and warmed up to room temperature, no reaction took place.

Another possible route for the preparation of a diazasulfonium ion is the methylation of an aminosulfilimine. Johnson et al. prepared an azasulfonium ion by methylation of a sulfilimine.[7] When an equimolar mixture of *N*-*p*-toluenesulfenylmorpholine and chloramine-T was refluxed in benzene,

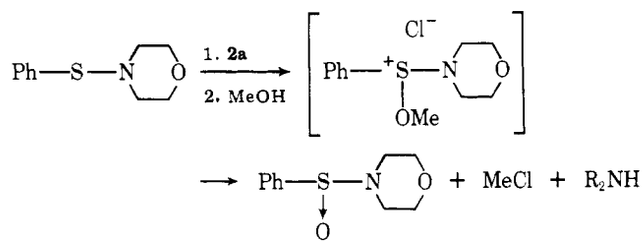


the corresponding sulfilimine was produced, which was treated with methyl trifluoromethanesulfonate and **3**. The corresponding diazasulfonium salt (**1g**) was obtained.

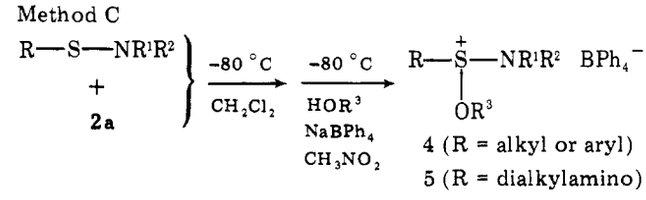
Azaoxasulfonium Ions. The azaoxasulfonium salt formed by the reaction of *N*-*p*-toluenesulfinylpyrrolidine and methyl triflate was stable only in methyl triflate, but those prepared by the treatment of *N*-benzenesulfinylmorpholine with methyl or ethyl triflate and **3** were isolable as stable high-melting crystals.[8] However, this alkylation method worked only when the amine group in sulfinamides was a cyclic secondary amine (morpholine or pyrrolidine) and R was methyl or ethyl. Thus, it is desirable to find a method which is generally applicable.



When methanol was added to a mixture of *N*-*p*-toluenesulfenylmorpholine and **2a** at −80 °C and then the solution was warmed up to room temperature, the following products were found. Since the reactions of alkoxymorpholinosulfonium ions with nucleophiles (methyl sulfide and tertiary amines) were exclusively the dealkylation from the alkoxy groups,[8] the above results are most reasonably explained by assuming the formation of methoxymorpholino-*p*-tolylsulfonium ion, which is attacked by chloride ion at the methyl carbon.



However, when **3** was added together with ROH to a mixture of a sulfenamide and **2a** at −80 °C, the anion was exchanged *at −80 °C* with tetraphenylborate ion which possesses no nucleophilicity, and the corresponding azaoxasulfonium salt was successfully isolated. The azaoxasulfonium salts (**4**) prepared are listed in Table I. This method appears to be applicable to various alcohols. It was possible to prepare **4d** from menthyl alcohol. This method was also applicable to phenols, and aryl salts (**4a,b,f**) were prepared.



Vilsmaier and Sprügel showed that the reaction of *S*-(*N*-succinimido)dimethylsulfonium ion with an amine yielded an azasulfonium ion, but its reaction with α-naphthol was different from that with an amine and yielded a naphthylsulfonium ion.[4] It is of interest to compare their findings with ours; the treatment of *N*-(2-propanesulfenyl)morpholine with **2a**, *p*-cresol, and **3** yielded **4b**. The use of **2b** in place of **2a** yielded no isolable products except amine salts.

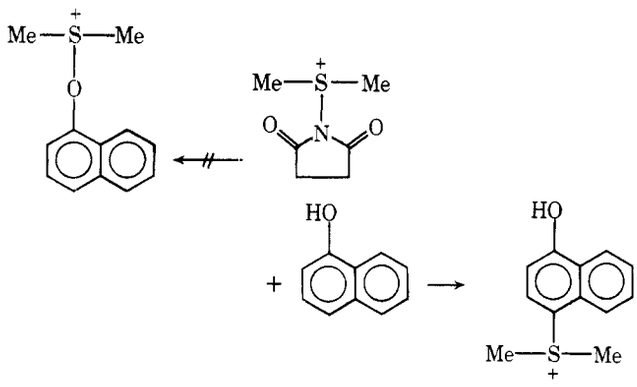
So far as we are aware, **4a,b,f** are the first examples of aryloxysulfonium ions; diarylaryloxysulfonium ions are unknown, and dialkylaryloxysulfonium ions cannot be isolated since they readily undergo a Sommelet-type rearrange-

Table I. Yields of Hetero-Substituted Sulfonium Salts

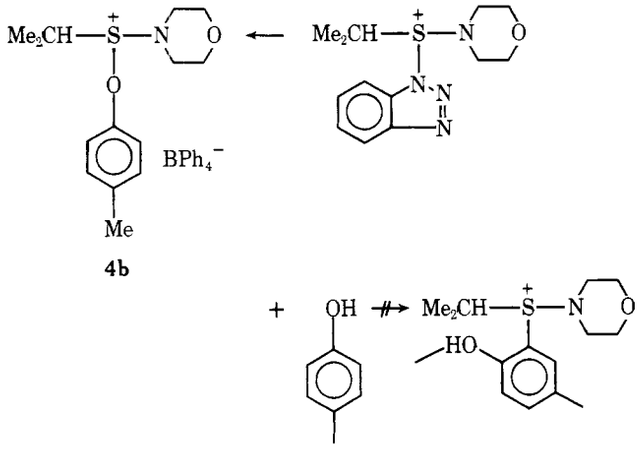
Method	Reactants	Registry no.			Registry no.		Products	Registry no.	Yield, %
A	$EtSN(CH_2CH_2)_2O$	24378-12-9	2a[b]	$HN(CH_2CH_2)_2O$	110-91-8	3[d]	$EtS^+N(CH_2CH_2)_2O$, BPh_4^- $N(CH_2CH_2)_2O$ (1a)	64520-81-6	60
A	$MeSN(CH_2CH_2)_2O$	4837-30-3	2a	$HN(CH_2CH_2)_2O$		3	$MeS^+N(CH_2CH_2)_2O$, BPh_4^- $N(CH_2CH_2)_2O$ (1b)	64520-83-8	65
A	$MeSN(CH_2CH_2)_2O$		2b[c]	$HN(CH_2CH_2)_2O$			1b		51
A	$MeSN(CH_2)_5$	7257-48-9	2a	$HN(CH_2)_5$	110-89-4	3	$MeS^+N(CH_2)_5$, BPh_4^- $N(CH_2)_5$ (1c)	64520-85-0	76
A	$MeSN(CH_2)_5$		2a	$HNEt_2$	109-89-7	3	$MeS^+N(CH_2)_5$, BPh_4^- NEt_2 (1d)	64520-87-2	70
A	$PhSNMe_2$	24380-79-8	2a	$HN(CH_2CH_2)_2O$		3	PhS^+NMe_2, BPh_4^- $N(CH_2CH_2)_2O$ (1e)	64508-82-3	91
A	p-$O_2NC_6H_4SN(CH_2CH_2)_2O$	40208-36-4	2a	$HNEt_2$		3	p-$O_2NC_6H_4S^+N(CH_2CH_2)_2O$, BPh_4^- NEt_2 (1f)	64520-89-4	63
A	$MeSN(CH_2)_5$		2a	$HNPh_2$	122-39-4	3	1c		25
B	p-TolS(=NTs)$N(CH_2CH_2)_2O$	64520-78-1		CF_3SO_3Me	333-27-7	3	p-TolS$^+N(CH_2CH_2)_2O$, BPh_4^- MeNTs (1g)	64520-91-8	62
C	$Me_2CHSN(CH_2CH_2)_2O$	64520-79-2	2a	HOPh	108-95-2	3	$Me_2CHS^+N(CH_2CH_2)_2O$, BPh_4^- OPh (4a)	64520-93-0	33
C	$Me_2CHSN(CH_2CH_2)_2O$		2a	HOC_6H_4Me-p	106-44-5	3	$Me_2CHS^+N(CH_2CH_2)_2O$, BPh_4^- OC_6H_4Me-p (4b)	64520-95-2	14
C	p-TolSN$(CH_2CH_2)_2O$	35390-53-5	2a	HOMe	67-56-1	3	p-TolS$^+N(CH_2CH_2)_2O$, BPh_4^- OMe (4c)	64520-97-4	82
C	p-TolSN$(CH_2CH_2)_2O$		2a	1-Menthol	2216-51-5	3	p-TolS$^+N(CH_2CH_2)_2O$, BPh_4^- O-menthyl (4d)	64535-88-2	47
C	p-TolSNMeCH_2Ph	64520-80-5	2a	HOMe		3	p-TolS$^+$NMeCH_2Ph, BPh_4^-	64520-99-6	10

C	*p*-TolSN(CH_2CH_2)$_2$O		2a	HOC_6H_4Me-*p*		3	OMe (4e) *p*-TolS$^+$N(CH_2CH_2)$_2$O, BPh_4^-	64508-65-2	38
C	O(CH_2CH_2)$_2$NSN(CH_2CH_2)$_2$O	5038-11-9	2a	$HOCH_2C(CH_3)_3$	75-84-3	3	OC_6H_4Me-*p* (4c) O(CH_2CH_2)$_2$NS$^+$N(CH_2CH_2)$_2$O, BPh_4^-	64508-67-4	60
C	O(CH_2CH_2)$_2$NSN(CH_2CH_2)$_2$O		2a	$HOCH_2CH_2OH$	107-21-1	3	$OCH_2C(CH_3)_3$ (5a) O(CH_2CH_2)$_2$NS$^+$N(CH_2CH_2)$_2$O, BPh_4^-	64508-69-6	51
C	O(CH_2CH_2)$_2$NSN(CH_2CH_2)$_2$O		2a	HOC_6H_4Me-*p*		3	OCH_2CH_2OH (5b) O(CH_2CH_2)$_2$NS$^+$N(CH_2CH_2)$_2$O, BPh_4^-	64508-71-0	45
C	O(CH_2CH_2)$_2$NSN(CH_2CH_2)$_2$O		2a	$HOCHMe_2$	67-63-0	3	OC_6H_4Me-*p* (5c) O(CH_2CH_2)$_2$NS$^+$N(CH_2CH_2)$_2$O, BPh_4^-	64508-73-2	37
C	Et_2NSNEt_2	3768-61-4	2a	$HOCHMe_2$		3	$OCHMe_2$ (5d) $Et_2NS^+NEt_2$, BPh_4^-	64521-06-8	38
A	$(CH_2)_5NSN(CH_2)_5$	25116-80-7	2a	$HN(CH_2)_5$		3	$OCHMe_2$ (5e) $(CH_2)_5NS^+N(CH_2)_5$, BPh_4^-	58357-09-8	82
A	O(CH_2CH_2)$_2$NSN(CH_2CH_2)$_2$O		2a	HN(CH_2CH_2)$_2$O		3	$N(CH_2)_5$ (6a) O(CH_2CH_2)$_2$NS$^+$N(CH_2CH_2)$_2$O, BPh_4^-	58357-03-2	71
D	O(CH_2CH_2)$_2$NSN(CH_2CH_2)$_2$O		2a	$ClN(CH_2CH_2)_2O$	23328-69-0	3	$N(CH_2CH_2)_2O$ (6b) 6b		52
A	O(CH_2CH_2)$_2$NSN(CH_2CH_2)$_2$O		2a	$HN(CH_2)_5$		3	O(CH_2CH_2)$_2$NS$^+$N(CH_2CH_2)$_2$O, BPh_4^-	58357-05-4	50
A	Et_2NSNEt_2		2a	HN(CH_2CH_2)$_2$O		3	$N(CH_2)_5$ (6c) $Et_2NS^+NEt_2$, BPh_4^-	64508-75-4	88
A	O(CH_2CH_2)$_2$NSN(CH_2CH_2)$_2$O		2a	HNMePh		3	$N(CH_2CH_2)_2O$ (6d) O(CH_2CH_2)$_2$NS$^+$N(CH_2CH_2)$_2$O, BPh_4^-	58357-01-0	62
A	O(CH_2CH_2)$_2$NSN(CH_2CH_2)$_2$O		2a	$HNEt_2$		3	NMePh (6e) O(CH_2CH_2)$_2$NS$^+$N(CH_2CH_2)$_2$O, BPh_4^-	64508-77-6	51
A	Et_2NSNEt_2		2a	$HNEt_2$		3	NEt_2 (6f) $Et_2NS^+NEt_2$, BPh_4^-	65408-78-7	35
B	O(CH_2CH_2)$_2$NS(=NTs)N(CH_2CH_2)$_2$O	3249-59-0		CF_3SO_3Me		3	NEt_2 (6g) O(CH_2CH_2)$_2$NS$^+$N(CH_2CH_2)$_2$O, BPh_4^- MeNTs (6h)	64508-80-1	63

[a] Reactants were added in the order listed. Solvents used were CH_2Cl_2 for 1a–f and 6a–g, CH_2Cl_2–CH_3NO_2 for 4a–f and 5a–e and CH_3NO_2 for 1g and 6h. Reactants were mixed at −80 °C, except those for methods B and D, which were mixed at room temperature. [b] Registry no.: 21050-95-3. [c] Registry no.: 128-09-6. [d] Registry no.: 143-66-8.

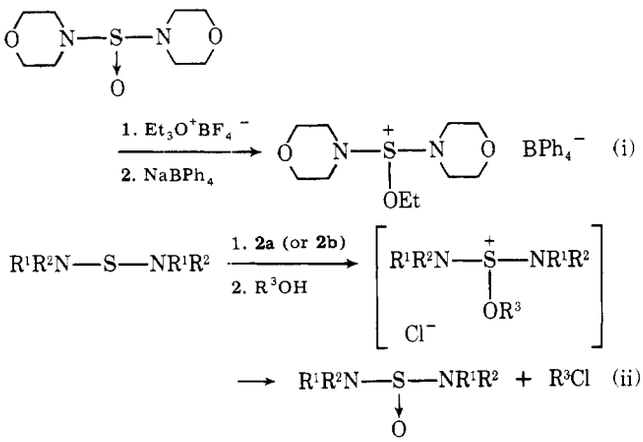


ment.[9,10] We attempted to prepare diphenylphenoxysulfonium salt by the reaction of phenyl sulfide with **2a** and *p*-cresol, but the desired sulfonium ion was not obtained.



4b

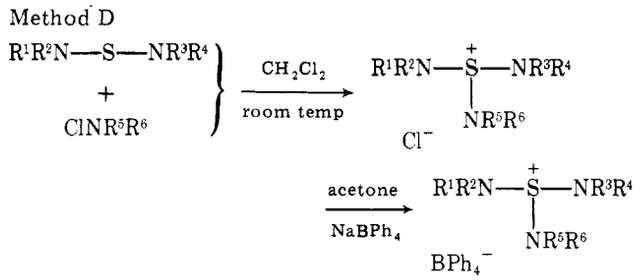
Diazaoxasulfonium Ions. The methods previously described for the preparation of diazaoxasulfonium ions were (i) alkylation of diamino sulfoxide[11] and (ii) reactions of diamino sulfides with **2a** and ROH.[12] Method i is not a general method for the preparation of diazaoxasulfonium ions, since it worked only with triethyloxonium tetrafluoroborate as the alkylating agent. Method ii was applicable to methanol, 2-propanol, and 2-methyl-2-propanol, but the diazaoxasulfonium ions formed could not be isolated.



In an attempt to find a method generally applicable to the preparation of various diazaoxasulfonium ions, method C was applied to this system; diazaoxasulfonium tetraphenylborates, **5a–e**, were successfully prepared.

It is of interest to note that method C is applicable to ethylene glycol, neopentyl alcohol, and *p*-cresol. **5c** is an example of the aryloxysulfonium salts which have not been described in the literature (except **4a,b,f** reported on in this paper).

Triazasulfonium Ions. Three methods have been found to be useful for the preparation of triazasulfonium salts (**6**): method A, reaction of a diamino sulfide with **2a** (or **2b**) followed by the treatment with a secondary amine and then with **3**[11] (preparation of **6a–g**); method B, alkylation of a diaminosulfilimine[13] followed by the treatment with **3** (preparation of **6h**); and method D, reaction of a diamino sulfide with an *N*-chloroamine (preparation of **6b**).



These triazasulfonium salts are very stable toward nucleophiles. For instance, when a CD_3NO_2 solution of **6b** and triphenylphosphine was heated at 100 °C for 1 day or when **6b** was refluxed in methanol for 1 day, no change was observed in its NMR spectrum. **6h** is an exception and decomposed to amine salts when heated with triphenylphosphine in CD_3NO_2 at 80 °C for 1 h.

Recently, Dawson and Swern reported the preparation of iminosulfonium salts from the reaction of a sulfide with **2a** (or **2b**) and a *primary* amine.[14] However, when syntheses of **4** or **6** containing a hydrogen atom on their nitrogen atoms were attempted using a primary amine, decomposition alway took place and amine salts were the main products. The instability of such azaoxa- and triazasulfonium ions is probably ascribable to the elimination of an alcohol or an amine from the sulfonium ion because of the presence of a labile hydrogen on its nitrogen atom and a labile alkoxy or amino group on the adjacent sulfur atom.

Experimental Section

Materials. *N*-Methanesulfenylmorpholine was prepared from methyl disulfide, chlorine gas, and morpholine[15] [bp 52–54 °C (6.5 mm); lit.[16] 48–49 °C (5 mm)]. Other sulfenamides were prepared in a similar manner:[15] *N*-ethanesulfenylmorpholine [bp 42.5–45 °C (2 mm)], *N*-methanesulfenylpiperidine [bp 59–61 °C (13 mm)], *N*-*p*-toluenesulfenylmorpholine [bp 80 °C (4.5 mm), mp 39–42 °C], *N*-benzenesulfenylmorpholine [bp 65 °C (4.0 mm), mp 32–35 °C, lit.[16] mp 33–36 °C], *N,N*-dimethylbenzenesulfenamide [bp 80 °C (8.0 mm)], *N*-*p*-nitrobenzenesulfenylmorpholine [mp 87.5–89.0 °C, lit.[16] 89–91 °C), *N*-benzyl-*N*-methyl-*p*-toluenesulfenamide (mp 45–47.5 °C); *N*-(2-propanesulfenyl) morpholine [bp 77–80 °C (5 mm)].

N-(Phenylmethanesulfenyl)morpholine was prepared by refluxing a benzene solution (15 mL) of *N*-(phenylmethanesulfenyl)succinimide (10 mmol) and morpholine (10 mmol) for 12 h. After the succinimide formed was removed by washing with water, the benzene was evaporated off and the residue obtained was recrystallized from ethanol: yield 69%; mp 73.5–75 °C (lit.[17] 72–74 °C). Harpp and Back prepared this compound by the reaction of *N*-(phenylmethanesulfenyl)-phthalimide and morpholine.[17] Although their method and ours are equally effective, ours has one advantage; *N*-(phenylmethanesulfenyl)succinimide is readily prepared by refluxing an equimolar mixture of benzyl disulfide and *N*-bromosuccinimide in benzene for 40 min (90% yield),[18] whereas *N*-(phenylmethanesulfenyl)phthalimide must be prepared by a two-step synthesis from benzyl disulfide via phenylmethanesulfenyl chloride.

Diamino sulfides were prepared according to Blake's method:[19] Dimorpholino sulfide (mp 125–126 °C, lit.[19] 125–126 °C), bis(diethylamino) sulfide [bp 58 °C (5.5 mm), lit.[20] 85 °C (12 mm)], dipiperidino sulfide (mp 72–74 °C, lit.[19] 74 °C).

Attempt for Preparing Diethylamino Morpholino Sulfide. An ethereal solution (40 mL) of morpholine (0.1 mol) was added to an ethereal solution (70 mL) of phenyllithium (0.1 mol). To this solution was added an ethereal solution (40 mL) of diethylaminosulfenyl chloride[21] (0.078 mol) at 20 °C in 30 min. After the mixture was al-

lowed to stand for 2 h, lithium chloride was filtered off and the solvent removed. The NMR spectrum of the brown oil obtained showed that it contained diethylamino morpholino sulfide in about 80% yield. However, when the oil was distilled at 67–82 °C (1 mm), the contents of dimorpholino sulfide and bis(diethylamino) sulfide increased. When the oil was kept in a freezer, crystals of dimorpholino sulfide gradually appeared and disproportionation slowly proceeded. It was not possible to isolate pure diethylamino morpholino sulfide.

Preparation of 1e (Method A). A CH_2Cl_2 solution (5 mL) of *N,N*-dimethylbenzenesulfenamide (5 mmol), a CH_2Cl_2 solution (5 mL) of **2a** (5 mmol), and a CH_2Cl_2 solution (3 mL) of morpholine (5 mmol) were placed separately in a glass vessel composed of three compartments connected to a vacuum line. After a freeze–thaw cycle was repeated twice, the first two solutions were mixed at −80 °C. The mixture was pale yellow, but when the amine solution was added to the mixture it became colorless. After the solution was allowed to warm up to room temperature, it was added to an acetone solution (20 mL) of $NaBPh_4$ (5 mmol). White precipitates which formed (NaCl) were filtered, and the addition of ether gave white crystals, which were found to be a 1:1 complex of **1e** and acetone: yield 91%; IR (KBr) 1720 cm^{-1}; NMR (CD_3SOCD_3) δ 2.10 [s, 6, $(CH_3)_2CO$], 3.06 [s, 6, $(CH_3)_2N$], 3.35–3.58 (m, 4, NCH_2CH_2O), 3.66–3.90 (m, 4, NCH_2CH_2O), 6.70–7.30 (m, 20, BPh_4), and 7.74 ppm (s, 5, PhS). Anal. Calcd for $C_{39}H_{45}BN_2O_2S$: C, 75.96; H, 7.36; N, 4.54. Found: C, 75.72, 75.77; H, 7.49, 7.52; N, 4.40, 4.42. This 1:1 complex formation was observed only when R is an aryl group, and no such complex was formed when R is an electron-releasing alkyl group (Me or Et). The complex did not lose the acetone under vacuum (10^{-4} mm, 25 °C, 6 h), but when the complex was heated up to 185 °C it melted at 182.5–183.6 °C; NMR the same as that of the complex except the loss of the δ 2.10 singlet; IR no 1720-cm^{-1} band. Anal. Calcd for $C_{36}H_{39}BN_2OS$: C, 77.41; H, 7.04; N, 5.02. Found: C, 77.35; H, 7.12; N, 4.90.

Other diazasulfonium salts were prepared in a similar manner. **1a:** yield 60%; mp 220–221 °C; Anal. Calcd for $C_{34}H_{41}BN_2O_2S$: C, 73.90; H, 7.48; N, 5.03. Found: C, 74.32; H, 7.70; N, 5.03. **1b:** yield 65%; mp 220–222 °C; Anal. Calcd for $C_{33}H_{39}BN_2O_2S$: C, 73.59; H, 7.30; N, 5.20. Found: C, 74.37; H, 7.44; N, 5.19. **1c:** yield 76%; mp 208–209 °C; Anal. Calcd for $C_{35}H_{43}BN_2S$: C, 78.64; H, 8.10; N, 5.24. Found: C, 78.56; H, 8.27; N, 5.21. **1d:** yield 70%; mp 217–218 °C; Anal. Calcd for $C_{34}H_{43}BN_2S$: C, 78.14; H, 8.29; N, 5.36. Found: C, 78.15; H, 8.58; N, 5.30. **1f:** yield 63%; mp 181–184 °C (dec).

Elemental Analyses. The results of C, H, N analyses of **1f, 4d–f, 5d,e,** and **6g** were somewhat removed from the theoretical values, but their NMR spectra were consistent with their structures.

Preparation of 1a by Exchange of the Anion of the Salt Prepared by Richards and Tarbell. An aqueous solution (10 mL) of ethyldimorpholinosulfonium tetrafluoroborate[2] (0.26 mmol) was added drop by drop to an aqueous solution (10 mL) of $NaBPh_4$ (0.25 mmol), and the white precipitates formed were filtered and dried, yield 83%. It NMR spectrum and melting point were the same as those of **1a** prepared by method A.

Preparation of 1g by Methylation of a Sulfilimine (Method B). A mixture of *N-p*-toluenesulfenylmorpholine (10 mmol), chloramine-T (10 mmol), pyridine (0.5 mL), and benzene (50 mL) was refluxed for 5 h, and the sodium chloride formed was filtered off. Concentration of the filtrate yielded the corresponding sulfilimine (81%). The sulfilimine (2.28 mmol) was stirred with methyl triflate (2.13 mmol) in nitromethane (30 mL) for 1 day at room temperature, and then a nitromethane solution (15 mL) of **3** (2.1 mmol) was added. After the solution was stirred for 0.5 h, ether was added. The crystals obtained were purified by recrystallization from acetone–ether (62%), mp 117–118 °C. Anal. Calcd for $C_{43}H_{45}BN_2O_3S_2$: C, 72.46; H, 6.37; N, 3.93. Found: C, 72.34; H, 6.87; N, 3.95.

Reaction of *N*-Benzenesulfenylmorpholine with 2a and Methanol. A CH_2Cl_2 solution (10 mL) of *N*-benzenesulfenylmorpholine (3.2 mmol) and a CH_2Cl_2 solution (15 mL) of **2a** (3.2 mmol) were mixed at −80 °C. When a CH_2Cl_2 solution (10 mL) of methanol (3.75 mmol) was added to this yellow solution at −80 °C it became colorless. After the solution was warmed up to room temperature its NMR spectrum was determined, which showed that the sulfenylmorpholine and methanol were quantitatively converted to *N*-benzenesulfinylmorpholine [δ 2.95–3.22 (m, 4, NCH_2), 3.60–3.90 (m, 4, OCH_2), 7.45–7.70 (m, 5, C_6H_5)] and methyl chloride (δ 2.96, s, 3), respectively.

Preparation of 4a (Method C). A cooled (−80 °C) CH_2Cl_2 solution (15 mL) of **2a** (6.2 mmol) was added to a CH_2Cl_2 solution (15 mL) of *N*-(2-propanesulfenyl)morpholine (6.2 mmol) at −80 °C. To this pale-yellow solution of a cooled CH_3NO_2 solution (20 mL) of phenol (6.2 mmol) and **3** (6.2 mmol) was added. After the mixture was stirred for 1 h it was allowed to warm up to room temperature. Addition of ether precipitated a mixture of **4a** and NaCl, which was separated and dissolved in acetone for removal of NaCl. Recrystallization from acetone–ether gave white crystals of **4a:** yield 33%; mp 131–132 °C; NMR (CD_3COCD_3) δ 1.60, 1.78 [d, 6, $(CH_3)_2CH$–], 3.74 (s, 8, NCH_2CH_2O), 4.35–5.00 [m, 1, $(CH_3)_2CH$–], 6.75–7.60 (m, 20, BPh_4), and 7.50–7.52 (s, 5, OPh). Anal. Calcd for $C_{37}H_{40}BNO_2S$: C, 77.47; H, 7.03; N, 2.44. Found: C, 77.53; H, 7.18; N, 2.54.

Other azaoxasulfonium salts were prepared in a similar manner. **4b:** yield 14%; mp 117–118 °C (dec). Anal. Calcd for $C_{38}H_{42}BNO_2S$: C, 77.67; H, 7.21; N, 2.38. Found: C, 77.59; H, 7.21; N, 2.37. **4c:** yield 82%; mp 149–150 °C. Anal. Calcd for $C_{36}H_{38}BNO_2S$: C, 77.27; H, 6.84; N, 2.56. Found: C, 77.37; H, 7.06; N, 2.74. **4d:** yield 47%; mp 118–120 °C; $[\alpha]^{24}_D$ −36.0 [*c* 2, acetone]. **4e:** yield 10%; mp 186–188 °C (dec). **4f:** yield 38%; mp 236–237 °C.

Preparation of 5a (Method C). A CH_2Cl_2 solution (15 mL) of **2a** (3.0 mmol), a CH_2Cl_2 solution (15 mL) of dimorpholino sulfide (3.0 mmol), and a CH_3NO_2 solution (15 mL) of neopentyl alcohol (3.0 mmol) and **3** (3.0 mmol) were treated in a manner similar to that described above for the preparation of **4a.** Recrystallization from acetone–ether–hexane gave white crystals of **5a:** yield 60%; mp 125–127 °C (dec). Anal. Calcd for $C_{37}H_{47}BN_2O_3S$: C, 72.77; H, 7.76; N, 4.59. Found: C, 72.60; H, 7.80; N, 4.57. **5b–e** were prepared in a similar manner. **5b:** yield 51%; mp 108.5–110.0 °C (dec). Anal. Calcd for $C_{34}H_{41}BN_2O_4S$: C, 69.85; H, 7.07; N, 4.71. Found: C, 69.39; H, 7.00; N, 4.69. **5c:** yield 45%; mp 236–237 °C. Anal. Calcd for $C_{39}H_{43}N_2O_3SB$: C, 74.28; H, 6.87; N, 4.44. Found: C, 74.10; H, 7.39; N, 4.25. **5d:** yield 37%; mp 118 °C (dec). **5e:** yield 38%; mp 196–199 °C (dec).

Preparation of 6a (Method A). In a manner similar to that described for the preparation of **1e,** a CH_2Cl_2 solution (10 mL) of dipiperidino sulfide (2.5 mmol) and a CH_2Cl_2 solution (10 mL) of **2a** (2.5 mmol) were mixed at −80 °C, and then a CH_2Cl_2 solution (10 mL) of piperidine (2.6 mmol) was added. After the mixture was warmed up to room temperature, an acetone solution (10 mL) of sodium tetraphenylborate (2.5 mmol) was added to the mixture and then the sodium chloride which precipitated was filtered. Upon addition of ether, crystals of **6a** precipitated, which were recrystallized from acetone–ether: yield 82%; mp 224.5–225.0 °C. Anal. Calcd for $C_{39}H_{50}BN_3S$: C, 77.59; H, 8.35; N, 6.96. Found: C, 77.38; H, 8.49; N, 6.62. **6c–f** were prepared in a similar manner. **6c:** yield 50%; mp 212.5–213.5 °C. Anal. Calcd for $C_{37}H_{46}BN_3O_2S$: C, 73.13; H, 7.63; N, 6.92. Found: C, 72.83; H, 7.64; N, 6.65. **6d:** yield 88%; mp 209.5–210.5 °C. Anal. Calcd for $C_{36}H_{48}BN_3OS$: C, 74.33; H, 8.32; N, 7.23. Found: C, 74.15; H, 8.53; N, 7.20. **6e:** yield 62%; mp 186.5–187.5 °C. Anal. Calcd for $C_{39}H_{44}BN_3O_2S$: C, 74.39; H, 7.04; N, 6.67. Found: C, 74.48; H, 7.39; N, 6.83. **6f:** yield 51%; mp 195–196 °C. Anal. Calcd for $C_{36}H_{46}BN_3O_2S$: C, 72.59; H, 7.78; N, 7.06. Found: C, 71.99; H, 7.58; N, 6.79. **6g:** yield 35%; mp 193.5–194.5 °C.

Preparation of 6b from *N*-Chloromorpholine (Method D). A CH_2Cl_2 solution (20 mL) of *N*-chloromorpholine (12 mmol) was added to a CH_2Cl_2 solution (20 mL) of dimorpholino sulfide (10 mmol) at room temperature, and the mixture was stirred for 1 day. Upon addition of carbon tetrachloride, white crystals of trimorpholinosulfonium chloride precipitated, which were recrystallized from dichloromethane: yield 52%; mp 131–132 °C.

An acetone solution (15 mL) of trimorpholinosulfonium chloride (2.37 mmol) was mixed with an acetone solution (15 mL) of $NaBPh_4$ (2.37 mmol). Upon addition of ether, a mixture of **6b** and NaCl precipitated, which was added to acetone and filtered. Ether was added to the filtrate, and crystals of **6b** precipitated: yield 69%; mp 210–211 °C. Anal. Calcd for $C_{36}H_{44}BN_3O_3S$: C, 70.92; H, 7.28; N, 6.89. Found: C, 71.31; H, 7.53; N, 6.84.

Preparation of 6h (Method B). *N-p*-Toluenesulfonyldimorpholinosulfilimine was prepared by the reaction of dimorpholino sulfide (10 mmol) with chloramine-T (10 mmol) in refluxing benzene (40 mL) in the presence of pyridine (0.2 mL);[13] recrystallization from $CHCl_3$–ether gave white crystals: yield 60%; mp 146–148 °C.

This sulfilimine (2.0 mmol) was stirred with methyl triflate (2 mmol) in nitromethane (15 mL) for 5 h at room temperature, and then a nitromethane solution (15 mL) of **3** (2.0 mmol) was added. After the mixture was stirred for 0.5 h ether was added. White precipitates which formed (**6h** and CF_3SO_3Na) were filtered and extracted with acetone. Addition of ether to the acetone extracts gave white needles of **6h:** yield 63%; mp 123–124 °C. Anal. Calcd for $C_{40}H_{46}BN_3O_4S_2$: C, 67.88; H, 6.57; N, 5.94. Found: C, 67.40; H, 7.06; N, 5.53.

Registry No.—*N*-Benzenesulfenylmorpholine, 4837-31-4; *N*-(phenylmethanesulfenyl)morpholine, 7257-55-8; *N*-(phenylmethanesulfenyl)succinimide, 14204-23-0; **1e** acetone complex, 64508-83-4; ethyldimorpholinosulfonium tetrafluoroborate, 24407-43-0; *N*-ben-

zenesulfinylmorpholine, 16066-32-3; trimorpholinosulfonium chloride, 64508-84-5.

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Imidazo[1,2-*a*]pyridine 1-Oxide. Synthesis and Chemistry of a Novel Type of *N*-Oxide

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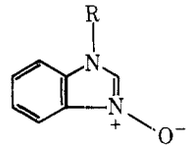
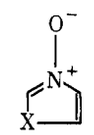
2-Phenylimidazo[1,2-*a*]pyridine 1-oxide, the first *N*-oxide of the polyazaindenes with the oxide function in the π-excessive five-membered ring, has been prepared. In contrast to the π-deficient *N*-oxides, back-bonding of the oxygen appears to be minimal. Some transformations of this compound are described.

The chemistry of π-deficient heterocyclic *N*-oxides has been the subject of numerous studies for many years. In contrast, much less is known about π-excessive heterocyclic *N*-oxides. Among the few representatives of this class of *N*-oxides are compounds of the general types A and B.[1,2] No *N*-oxides

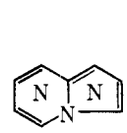


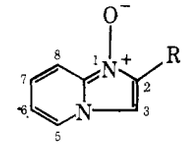
A



B, X = O, S, NR

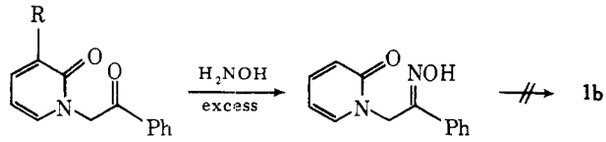
of the π-excessive five-membered ring in the nitrogen-bridged polyazaindenes are known. We now wish to describe the synthesis and some chemical reactions of a member of this class of heterocyclic *N*-oxides, imidazo[1,2-*a*]pyridine 1-oxide (**1b**).





1a, R = H
b, R = Ph

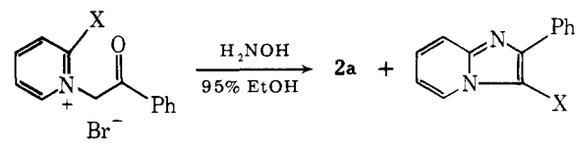
Since earlier work in our laboratory had shown that direct N-oxidation of imidazo[1,2-*a*]pyridines with peracids leads to cleavage of the five-membered ring,[3] we approached the *N*-oxide synthesis by indirect intramolecular cyclizations. When compound **2a**, obtained either by alkylation of 2-pyridone[4] or preferably by base hydrolysis of the pyridinium salts **4** (X = Cl, Br), is treated with hydroxylamine under acidic or neutral conditions, the reactions stop at the oxime stage, high yields of *syn*- and *anti*-oximes **3** being formed. The mixtures, largely the undesired anti isomer with respect to the phenyl substituent,[5] are stable at the melting point and thus not thermally convertible to the *N*-oxide **1b**.



2a, R = H

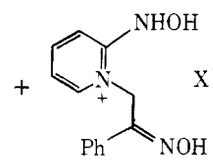
3 syn + anti

An attempt to prepare compound **1b** by reaction of the pyridinium salt **4** with hydroxylamine in 95% ethanol also gave



4a, X = Cl
b, X = Br

5, X = H
6a, X = Br
b, X = Cl



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none of the desired product, but rather a mixture containing the pyridone **2a** (55%) and compounds **5** (8%) and **6a** and **6b** (3%). Another component had IR and mass spectral properties consistent with structure **7**. The formation of the imidazo[1,2-*a*]pyridines **5**, **6a**, and **6b** suggests that cyclization to the *N*-oxide **1b** may indeed have occurred, but that this compound is not stable under the reaction conditions. Further, formation of the pyridone **2a** implicates hydroxylamine in the hydrolysis of the pyridinium salt **4**, either as a general base catalyst or as a nucleophile.[6]

The reaction was therefore repeated under strictly anhydrous conditions in the presence of the hydroxylamine hydrochloride. Under these reaction conditions, the product

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