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BASE-INITIATED ELIMINATION REACTIONS OF N-ARYLSULFONOXYSULFONAMIDES

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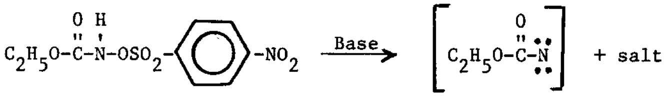
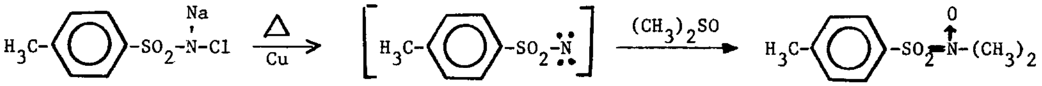
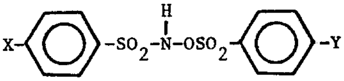
Nitrenes are neutral, electrophilic species, $\mathrm{R{-}\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}}$, isoelectronic with carbenes and they show similar reactivity (1-4). Photolysis and thermolysis of azides are the most important nitrene-generating methods and have been used, for example, to obtain carboalkoxynitrenes (3,4) and sulfonylnitrenes (2,5). α-Elimination reactions have also been used to generate nitrenes (or nitrene-transfer agents); two procedures are the base-induced elimination reaction of *p*-nitrobenzenesulfonoxyurethane (4) and the copper-catalyzed thermal decomposition of chloramine-T(6):





For some time we have been preparing compounds suitably constructed to serve as nitrene precursors by base-initiated α-elimination. Such elimination reactions require a substrate, $\mathrm{A{-}\underset{H}{\underset{|}{N}}{-}B}$, in which (a) the proton is relatively acidic, (b) B is an efficient leaving group, and (c) the nitrene species, $\mathrm{A{-}\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}}$, has reasonable stability and can be trapped before it decomposes or rearranges. An excellent example of a suitable structure has been described by Lwowski(4) who generated carbethoxynitrene by reaction of *p*-nitrobenzenesulfonoxyurethane with base, illustrated above, and studied reactions of the nitrene in detail.

Sulfonylnitrenes are also relatively stable and trappable and we are seeking ways to generate them nonphotolytically by α-elimination reactions. We are now reporting the presumed generation of sulfonylnitrenes from N-arylsulfonoxysulfonamides (I), species of the $\mathrm{A{-}\underset{H}{\underset{|}{N}}{-}B}$ class, in which A is the benzenesulfonyl or *p*-methylbenzenesulfonyl group and B is the benzenesulfonoxy or *p*-nitrobenzenesulfonoxy group. Since both A and B are electron-withdrawing, the proton is acidic and can be titrated, unstable salts are readily formed and, in the presence of dimethyl sulfide or sulfoxide and base, I presumably yield sulfonylnitrenes that can be trapped.



		MP, °C	Yield, %(7)
Ia:	X=H, $Y=NO_2$(8)	179-180	72
b:	$X=CH_3$, $Y=NO_2$	186	70
c:	X=H, Y=H	159-161	48

Ia-c are prepared from arylsulfonhydroxamic acids (1 mole), arylsulfonyl chlorides (1 mole) and triethyl amine (preferred) (3-4 moles) or pyridine as the acid-acceptors. With triethyl amine, the amine hydrochloride and amine salts of I are obtained in high yield; acidification yields I.

Amine salts of I are unstable even at low temperatures and should be acidified promptly; at room temperature, for example, they are converted to black tars within hours or days and decompose at their melting points. With pyridine as the acid-acceptor yields of I are substantially lower than those given above. Also Ia can be prepared from sodium benzenesulfonhydroxamate and p-nitrobenzenesulfonyl chloride in chloroform but yields are poor.

Salts of Ia,b,c

Base	Ia, MP, °C	Yield, %	Ib, MP, °C	Yield, %	Ic, MP, °C	Yield, %
Triethyl amine	75.5 (dec.)	93	61 (dec.)	--	73 (dec.)	72
N-Methylmorpholine	82 (dec.)	87	79 (dec.)	92	---	--
Pyridine	103 (dec.)	90	92-93 (dec.)	88	---	--

Ia (3.58 g, 0.01 mole) yields a mixture of N-benzenesulfonyldimethylsulfilimine (IIa) and triethylammonium p-nitrobenzenesulfonate (III) upon refluxing for two hours suspended in dimethyl sulfide (25 g, 0.415 mole) to which triethylamine (1.50 g, 0.015 mole) had been added dropwise at the start. Evaporation of excess dimethyl sulfide yields a residue consisting of about equal parts of IIa and III [analyzed by nmr by comparing the integration ratio of the signal at 6.85 τ (methylene protons of III, 6H) with that at 7.32 τ (methyl protons of IIa, 6H)]. The yield of crude IIa is calculated to be 78% but after recrystallization of the crude mixture from methyl isobutyl ketone and three times from ethyl acetate, the yield of isolated IIa, mp 124-6°, is about 40%. IIa, IR (KBr, cm^{-1}): 3070, 1455, 1430, 1278, 1145, 1105, 1080, 1040, 980, 765, 712, 695. NMR (D_2O): 7.23 (s 6H), ca 2.20 τ (m, 4.9H)

Anal. calcd. for $C_8H_{11}NO_2S_2$: C 44.2; H 5.10; N 6.45; S 29.5

Found: C 44.1; H 4.93; N 6.29; S 29.6

A mixture melting point with authentic IIa, mp 130°, prepared from Chloramine B and dimethyl sulfide shows no depression and the ir spectra are virtually identical.

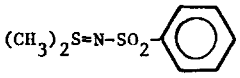
Similarly, reaction of Ib with dimethyl sulfide and triethyl amine yields N-(p-toluenesulfonyl)dimethylsulfilimine, IIb, mp 157-158° (36%).

IIb, IR (KBr, cm^{-1}): 3060, 1420, 1280, 1145, 1095, 1050, 1030, 1019, 955, 821, 758, 687.

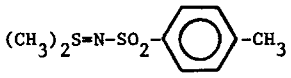
NMR (acetone-d_6): 7.62 (s, 3H), 7.23 (s, 6H), 2.61 (d, 2H), 2.25 τ (d, 2H).

A mixture melting point with authentic IIb, mp 158°, prepared from chloramine T and dimethyl sulfide (9) is undepressed.

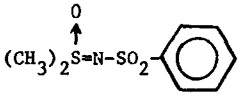
Reaction of Ia and Ib at 40-50° with dimethyl sulfoxide and triethyl amine gives low yields of N-benzenesulfonyldimethylsulfoximine (IIIa), mp 116-117°, and N-(p-toluenesulfonyl)-dimethylsulfoximine (IIIb), mp 166-167°, respectively. The ir spectra of IIIa and IIIb are essentially identical with those of authentic specimens prepared by oxidation of the corresponding sulfilimines (10) and mixture melting points show no depression.



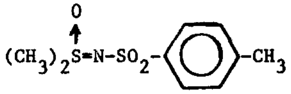
IIa, mp 124-126° (authentic sample 130°)



IIb, mp 157-158° (lit. 159°) (9)



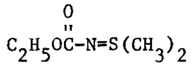
IIIa, mp 116-117° (lit. 115°) (10)



IIIb, mp 166-167° (lit. 167-169°) (10)

Two pathways have been considered for rationalization of the reaction products of I with dimethyl sulfide or sulfoxide and triethylamine, namely, a nitrene or a displacement pathway (1,2). Information available so far does not permit an unequivocal choice but the following experiment causes us to favor a nitrene (or nitrene-transfer) pathway.

Reaction of p-nitrobenzenesulfonoxyurethane (5.80 g, 0.02 mole) with dimethyl sulfide (31 g, 0.5 mole) and triethylamine (2.25 g, 0.022 mole) at 10° followed by refluxing two hours, then evaporation of excess dimethyl sulfide yields a residue consisting of an ether-insoluble and an ether-soluble fraction. The ether-insoluble fraction is triethylammonium p-nitrobenzenesulfonate, mp 118-120° (95% yield). The ether solution, after drying, is evaporated under vacuum to yield a brown liquid residue which can be decolorized with carbon in acetone solution. The insoluble liquid residue is identified as N-carbethoxydimethylsulfilimine (IV) (2.30 g, 73%) (11).



$$C_2H_5O\overset{O}{\overset{\|}{C}}-N{=}S(CH_3)_2$$

IV

Since it is generally agreed that carbethoxynitrene is a product of the reaction of *p*-nitrobenzenesulfonoxyurethane with triethylamine, and the sulfilimine isolated is the anticipated product of reaction of the nitrene with dimethyl sulfide, we feel that a nitrene (or nitrene-transfer) pathway is a reasonable one for the analogous reactions of I.

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7. Yields of I are for analytically pure compounds; crude yields are 10-20% higher but melting points are several degrees low. Correct elemental analyses have been obtained for I and for the arylsulfonhydroxamic acids. Ir and nmr spectra are consistent with the structures for all compounds.
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11. An authentic sample of IV is readily prepared by reaction of N-monochlorourethane with dimethyl sulfide followed by reaction of the intermediate salt with the stoichiometric quantity of base. D. Saika and D. Swern, unpublished.