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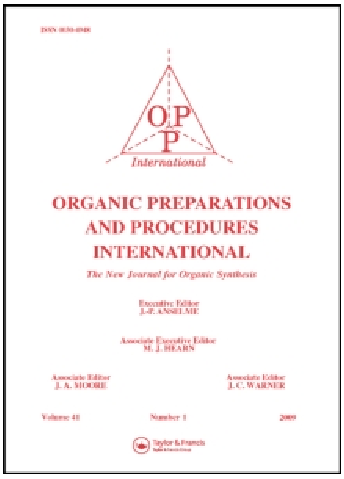

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N-SULFENYL - AND N-SULFINYLSULFOXIMIDES

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N-SULFENYL- AND N-SULFINYLSULFOXIMIDES

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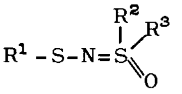

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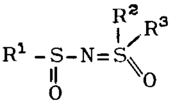
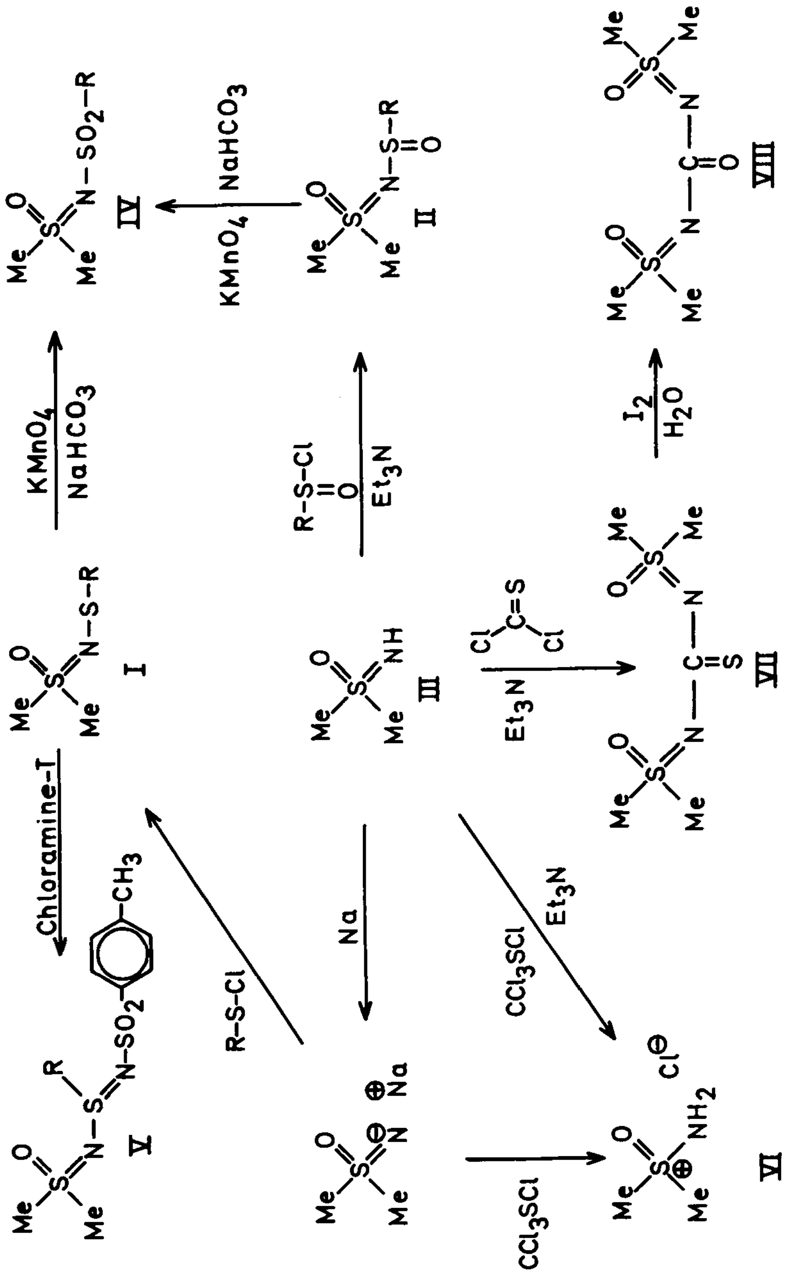


II

Although N-acyl-, N-sulfonyl[1]-, and N-phosphonylsulfoximides[2] are known, no study of organic N-sulfenylsulfoximides (I) or N-sulfinylsulfoximides (II) has appeared. Here, the preparations of I ($R^2 = R^3 = CH_3$, $R^1 = C_6H_5$) and II ($R^2 = R^3 = CH_3$, $R^1 = CCl_3$, C_6H_5) are reported. The compounds were characterized by their chemical reactions as shown in Scheme I.

S,S-Dimethyl-N-sulfinylsulfoximides (II) were readily accessible by the reaction of S,S-dimethylsulfoximide (III) and a sulfinyl chloride in the presence of a tertiary amine. The products are readily oxidized to S,S-dimethyl-N-sulfonylsulfoximides (IV) by basic potassium permanganate.

Treatment of the sodium salt of III with benzenesulfenyl chloride gave N-benzenesulfenyl-S,S-dimethylsulfoximide (I) which is readily oxidized to N-benzenesulfonyl-S,S-dimethylsulfoximide (IV) with permanganate. The structure of I was


I
II
III
IV
V
VI
VII
VIII
KMnO4
NaHCO3
R-S-Cl
Et3N
Chloramine-T
Na
CCl3SCl
I2
H2O
Me
N-S-R
N-SO2-R
NH
N-SO2
CH3
Cl⊖
NH2
C=S
C=O
Cl

Scheme I

further confirmed by its conversion to N-benzene(4-toluenesulfonylimino)sulfinyl-S,S-dimethylsulfoximide (V) with chloramine-T. The reaction of trichloromethanesulfenyl chloride with III or its sodium salt provided S,S-dimethylsulfoxonium chloride (VI) as the only isolated product.

With thiophosgene, III gave N,N'-bis(dimethylsulfoxylidene)thiourea (VII) in the presence of a base; iodine in boiling water hydrolyzed VII to the known N,N'-bis(dimethylsulfoxylidene)urea (VIII).

II ($R = CCl_3$) did not react with triphenylphosphine in boiling benzene.

The infrared stretching bands of the $-N{=}\overset{|}{\underset{|}{S}}{=}O$ group are shown in Table I. The asymmetric and symmetric bands of the S,S-dimethyl-N-sulfinylsulfoximides (1200-1190 cm^{-1} and 1040-1030 cm^{-1}) appear at lower wave numbers than those of the corresponding S,S-dimethyl-N-sulfonylsulfoximides (1230-1220 cm^{-1} and 1070-1060 cm^{-1}) or N-arene-S,S-dimethylsulfoximide[3] (1235 and 1090 cm^{-1}). This difference may be explained by an effective conjugation between the sulfinyl and the sulfoximide groups. Also, the stretching bands of the N-sulfenylsulfoximide (1198 and 1020 cm^{-1}) appear at lower wave numbers than with weakly conjugated compounds.

The melting points, analyses, and infrared spectral data are given in Table I.

TABLE I

Compound	m.p. °C	%C		%H		%N		%S		Infrared Spectral Data cm^{-1} (in KBr)	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	ν-N=S=O	
I R=C_6H_5		45.87	47.75	5.47	5.51	6.44	6.96	28.90	31.86	1198* 1020	
II R=CCl_3	101.5-103	13.77	13.94	2.50	2.34	5.31	5.42			1200 1040	ν_{SO}=1120
II R=C_6H_5	84-85.5	44.27	44.22	5.20	5.10			29.38	29.51	1190 1030	ν_{SO}=1086
IV R=CCl_3	152-154	13.12	13.12	2.22	2.20	5.20	5.10	23.20	23.35	1228 1072	ν_{SO_2}=1320 1138
V	112-114	48.66	48.62	4.96	4.90			26.75	25.97	1220 1035	ν_{SO_2}=1260 1134 $\nu_{S=N}$= 940
VI	118-120	18.16	18.52	6.24	6.22	10.44	10.81			1237 1045	
VII	204-206	26.32	26.30	5.38	5.30	12.08	12.27	41.88	42.12	1198 1000	

*neat

EXPERIMENTAL

S,S-Dimethyl-N-trichloromethanesulfinylsulfoxide (II, R = CCl_3). To a solution of 4.65 g (0.05 mole) S,S-dimethylsulfoximide[4] and 5.05 g (0.05 mole) triethylamine in 50 ml dry benzene was added, during 8 hours, 10.1 g (0.05 mole) trichloromethanesulfinyl chloride[5] in 50 ml benzene with stirring at room temperature. After the reaction mixture had been stirred for another 2 h, 6.2 g triethylamine hydrochloride was separated by filtration and the solution evaporated under reduced pressure to an oil which was dissolved in methylene chloride filtered, and placed in a refrigerator overnight. Large crystals were separated by filtration and recrystallized from ethyl acetate. Yield: 9.2 g (75%), m.p. 101.5-103°C. PMR in CD_3CN showed a singlet centered at $\delta = 3.38$ ppm (TMS as internal standard).

N-Benzenesulfinyl-S,S-dimethylsulfoximide (II, R = C_6H_5). To a solution of 4.65 g (0.05 mole) S,S-dimethylsulfoximide[4] and 5.05 g (0.05 mole) triethylamine in 50 ml benzene at 0° was added with stirring 8.02 g (0.05 mole) benzenesulfinyl chloride[6] during 2 hours. After another 2 hours at room temperature 6.9 g triethylamine hydrochloride was filtered off. The solution was evaporated *in vacuo* to an oil which crystallized on addition of a little ethyl acetate. The combined crops were recrystallized from ethyl acetate. Yield: 5.76 g (53%), m.p. 84-85.5°C.

N-Benzenesulfenyl-S,S-dimethylsulfoximide (I). To a slurry of 0.025 mole S,S-dimethyl-N-sodiosulfoximide in dry benzene was added 0.02 mole benzenesulfenyl chloride[7] with stirring at room temperature. After stirring for another hour the slurry was filtered, and the solution evaporated under reduced pressure to a yellow oil which was decolorized with charcoal in methylene chloride and evaporated. The crude product could be purified on an Al_2O_3 column by eluating with ether-ligroin. Crude yield: 96%. PMR in $CDCl_3$ showed a multiplet centered at 7.27 ppm and a singlet at $\delta = 3.11$ ppm.

S,S-Dimethyl-N-sulfonylsulfoximides (IV). 0.003 mole S,S-dimethyl-N-sulfinylsulfoximide and 0.002 mole potassium permanganate (respectively 0.003 mole S,S-dimethyl-N-sulfenylsulfoximide and 0.004 mole potassium permanganate) and a small amount of $NaHCO_3$ in 5 ml water was heated to boiling temperature in 5 minutes and cooled to 0°. The solid material was filtered off by suction and recrystallized from ethanol ($R = C_6H_5$) affording the following yields:

I → IV, ($R = C_6H_5$): 47%, m.p. 113.5-115° (lit.[8] 115°)
II → IV, ($R = C_6H_5$): 43%, m.p. 113-115° (lit.[8] 115°)
II → IV, ($R = CCl_3$): 88%, m.p. 152-154°

N-Benzene(4-toluenesulfonylimino)sulfinyl-S,S-dimethylsulfoximide (V). To 0.9 g (0.0045 mole) N-benzenesulfenyl-S,S-dimethylsulfoximide dissolved in 20 ml acetone was added a solution of 1.1 g Chloramine-T in 10 ml acetone and 6 ml water at room temperature. After half an hour at room temperature the solvent was evaporated *in vacuo*. The oily residue was treated with water several times and the white powder filtered off, dried, and recrystallized from ethyl acetate affording 1.13 g (68%), m.p. 112-114°.

Bis(dimethylsulfoxylidene)thiourea (*VII*). A solution of 8.3 g (0.072 mole) thiophosgene in 20 ml benzene was slowly added to 13.5 g (0.148 mole) S,S-dimethylsulfoximide and 14.7 g (0.147 mole) triethylamine in 100 ml benzene with stirring at 0°. Stirring was continued for 2 hours at room temperature. The precipitation was separated by filtration and was treated with methanol. Undissolved material was filtered off and recrystallized from N,N-dimethylformamide, m.p. 204-206°. Yield: 1.85 g (11%).

Bis(dimethylsulfoxylidene)urea (*VIII*). 0.228 g (0.001 mole) bis(dimethylsulfoxylidene)thiourea was dissolved by warming in 10 ml water and 0.128 g iodine dissolved in 5 ml ethanol was added. After stirring 1 hour at 50° the solution was cooled and filtered. The solution was neutralized with $NaHCO_3$, filtered and evaporated under reduced pressure. The crystalline solid then obtained was recrystallized from abs. ethanol to give 0.14 g (66%) of product, m.p. 187-189° (lit.[9] 189-191°).

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