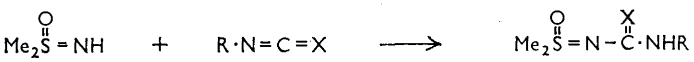
545. *Dimethylsulphoxylideneureas and Dimethylsulphoxylidenethioureas*

By Rudolf Wehr

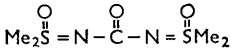
Several reactions of the recently discovered dimethylsulphoxime have been described.[1-3] Among these are the reactions with acetic anhydride to give *N*-acyldimethylsulphoximine [1] and the reaction with sodium to give *N*-sodium dimethylsulphoximine,[3] clearly demonstrating the acidity of the imine hydrogen in dimethylsulphoxime.

Dimethylsulphoxime should therefore react with alkyl isocyanates and similar compounds. Dimethylsulphoximine does react with alkyl isocyanates, alkyl isothiocyanates, alkylsulphonyl isocyanates, acyl isothiocyanates, isocyanic acid, and phosgene to give the expected *N*-dimethylsulphoxylidene-*N'*-alkyl- or -acyl-ureas (I), -thioureas (II), or bis-(dimethylsulphoxylidene)urea (III).



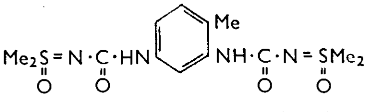
$$\mathrm{Me_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{=NH} \quad + \quad \mathrm{R{\cdot}N{=}C{=}X} \longrightarrow \mathrm{Me_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{=N-}\overset{\mathrm{X}}{\overset{\|}{\mathrm{C}}}\mathrm{{\cdot}NHR}$$

(I: X = O)
(II: X = S)



$$\mathrm{Me_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{=N-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-N=}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{Me_2}$$

(III)



(IV)

These substituted ureas and thioureas remain unchanged on being heated to 250° for several hours. The *N*-sulphoxylidene-*N'*-alkyl-ureas and -thioureas are soluble in hot water and hot ethanol. Bis(dimethylsulphoxylidene)urea and dimethylsulphoxylidene-urea are soluble in water at room temperature. The infrared spectra of these compounds show two strong $-C(=O)-N<$ absorption bands at 6·2—6·35 and 6·5—6·7 μ or one strong $-C(=S)-N<$ band at 6·5—6·7 μ; one medium-strong NH absorption at 2·95—3·2 μ, an $>S=O$ band at 9·0—9·7 μ (very strong), and an $>S=N$ band at 8·1—8·3 μ (very strong). Molecular-weight determinations gave the desired results.

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[1] Fernanda Misani, T. W. Fair, and L. Reiner, *J. Amer. Chem. Soc.*, **1951**, **73**, 459.

[2] H. R. Bentley, E. E. McDermott, and J. K. Whitehead, *Proc. Roy. Soc.*, **1951**, *B*, **138**, 265.

[3] J. K. Whitehead and H. R. Bentley, *J.*, 1952, 1572.

Experimental

Experimental.—Dimethylsulphoximine. The compound was prepared from dimethylsulphoxide, sodium azide, and sulphuric acid in chloroform.[2] On a three-mole scale dimethylsulphoximine, b. p. 100—102°/1·5 mm., m. p. 57—58°, was obtained in 65—75% yield. Careful temperature control is necessary during the distillation; the pot temperature should be kept under 150°. One distillation residue exploded when the temperature reached 180° at 5 mm. pressure.

N-*Dimethylsulphoxylidene*-N′-*alkyl*(-*acyl*, -*alkylsulphonyl*)-*ureas and -thioureas.* A total of 18·6 g. (0·2 mole) of dimethylsulphoximine and an alkyl (acyl, alkylsulphonyl) isocyanate or isothiocyanate (0·2 or 0·1 mole of tolylene-2,4-di-isocyanate; all compounds with the exception of methylsulphonyl isocyanate[4] and phenylsulphonyl isocyanate[5] are commercially available) were mixed and heated for 1 hr. on a steam-bath in a flask protected by a calcium chloride tube. A homogeneous melt was formed when the temperature reached 60°; the temperature of the mixture increased to 125—145° during the first 5—10 min. After cooling to room temperature, the solidified products were recrystallised from ethanol. The new compounds, so prepared are listed in the Table.

Dimethylsulphoxylideneurea. A solution of 16·2 g. (0·2 mole) of potassium cyanate and 18·6 g. (0·2 mole) of dimethylsulphoximine in 50 ml. of acetic acid was heated on a steam-bath for 1 hr. Evaporation *in vacuo* and recrystallisation from ethanol gave 15 g. of compound (I, R = H) m. p. 179—180°.

Sulphoxylideneureas and sulphoxylidenethioureas

				Found (%)					Calc. (%)			
Compd.	R	M. p.	Yield (%)[a]	C	H	N	S	Formula	C	H	N	S
(I)	Et	112—113°	85	36·6	7·35	16·6	19·9	$C_5H_{12}NO_2S$	36·55	7·35	17·1	19·6
(II)	Et	106—107	75	33·3	6·55	15·55	36·0	$C_5H_{12}NOS_2$	33·3	6·7	15·6	35·6
(I)	n-C_8H_{17}	90—91	70	53·05	9·7	11·8	12·95	$C_{11}H_{24}NO_2S$	53·2	9·75	11·2	12·9
(I)	C_6H_5	186—187	95	51·0	5·75	13·0	15·1	$C_9H_{12}NO_2S$	51·0	5·65	13·2	15·1
(II)	C_6H_5	168—169	85	47·4	5·3	12·25	28·05	$C_9H_{12}NOS_2$	47·4	5·3	12·3	28·1
(I)	*o*-C_6H_4Me	130—131	75	—	—	12·5	—	$C_{10}H_{14}NO_2S$	—	—	12·4	—
(I)	*m*-C_6H_4Me	128—129	75	—	—	12·45	—	$C_{10}H_{14}NO_2S$	—	—	12·4	—
(I)	*p*-C_6H_4Me	188—189	60	—	—	12·15	—	$C_{10}H_{14}NO_2S$	—	—	12·4	—
(I)	*o*-C_6H_4Cl	114—115	87	—	—	11·45	—	$C_9H_{11}ClNO_2S$	—	—	11·4	—
(I)	*m*-C_6H_4Cl	159—160	50	—	—	11·35	—	$C_9H_{11}ClNO_2S$	—	—	11·4	—
(I)	*p*-C_6H_4Cl	226—227	80	—	—	11·5	—	$C_9H_{11}ClNO_2S$	—	—	11·4	—
(I)	2,5-$C_6H_3Cl_2$	152—153	85	—	—	10·25	—	$C_9H_{10}Cl_2NO_2S$	—	—	10·0	—
(I)	3,4-$C_6H_3Cl_2$	194—195	85	—	—	10·2	—	$C_9H_{10}Cl_2NO_2S$	—	—	10·0	—
(I)	3,5-$C_6H_3Cl_2$	183—184	80	—	—	10·3	—	$C_9H_{10}Cl_2NO_2S$	—	—	10·0	—
(I)	*o*-C_6H_4OEt	96—97	70	—	—	11·35	—	$C_{11}H_{16}NO_3S$	—	—	10·9	—
(I)	*p*-C_6H_4OEt	167—168	50	—	—	11·15	—	$C_{11}H_{16}NO_3S$	—	—	10·9	—
(I)	*o*-$C_6H_4NO_2$	165—166	70	—	—	16·3	—	$C_9H_{11}N_2O_4S$	—	—	16·3	—
(I)	*m*-$C_6H_4NO_2$	147—148	75	—	—	16·55	—	$C_9H_{11}N_2O_4S$	—	—	16·3	—
(I)	*p*-$C_6H_4NO_2$	260—265	60[b]	42·4	4·4	16·1	12·65	$C_9H_{11}N_2O_4S$	42·1	4·3	16·3	12·5
(I)	1-Naphthyl	134—136	70	59·6	5·45	11·3	—	$C_{13}H_{14}NO_2S$	59·5	5·4	10·6	—
(II)	1-Naphthyl	154—156	70	56·5	5·3	10·1	23·3	$C_{13}H_{14}NOS_2$	56·1	5·05	10·1	23·0
(I)	2-Naphthyl	165—166	60	—	—	10·3	—	$C_{13}H_{14}NO_2S$	—	—	10·6	—
(I)	SO_2Me	160—162	50	22·45	4·7	12·95	29·35	$C_4H_{10}NO_4S_2$	22·4	4·7	13·1	29·9
(I)	$SO_2C_6H_5$	150—151	60	39·55	4·45	10·2	23·15	$C_9H_{12}NO_4S_2$	39·2	4·4	10·1	23·2
(II)	*p*-$CO{\cdot}C_6H_5Br$	168—170	50	35·45	3·2	8·8	19·4	$C_{10}H_{12}BrNO_2S_2$	35·8	3·2	8·4	19·1
(I)	H	179—180	55	25·95	5·5	19·5	23·2	$C_3H_8NO_2S$	26·4	5·9	20·6	23·5
(III)	—	189—191	45	28·0	5·7	13·35	29·85	$C_5H_{12}N_2O_2S_2$	28·3	5·7	13·2	30·2
(IV)	—	218—220	35[c]	42·75	5·55	15·1	17·8	$C_{13}H_{20}N_4O_4S_2$	43·3	5·6	15·6	17·8

[a] After recrystallisation from ethanol. [b] Recrystallised from 80% aqueous dimethylformamide. [c] Recrystallised from 20% aqueous ethanol.

Bis(*dimethylsulphoxylidene*)*urea.* To a stirred and ice-bath-cooled solution of 18·6 g. (0·2 mole) of dimethylsulphoximine and 20·5 g. (0·2 mole) of triethylamine in 100 ml. of acetone was added a solution of 10·0 g. (0·1 mole) of phosgene in 50 ml. of acetone over ½ hr. The mixture was subsequently stirred for 2 hr. at room temperature, evaporated on a steam-bath, and the residue recrystallised from 500 ml. of ethanol to give 9·5 g. of compound (III), m. p. 189—191°.

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[*Received, July* 31*st*, 1964.]

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[4] O. C. Billeter, *Ber.*, 1905, **38**, 2013.

[5] O. C. Billeter, *Ber.*, 1904, **37**, 690.