SYNTHESIS AND STRUCTURE OF THE DIMETHYLAMIDE OF CHLOROTHIOFORMIC ACID AND ITS REACTION WITH POTASSIUM THIOCYANATE

A. N. Pudovik, V. K. Khairullin,
M. A. Vasyanina, R. M. Kamalov, O. N. Kataeva,
I. A. Litvinov, and V. A. Naumov

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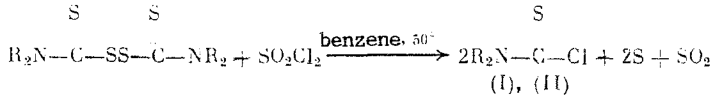
Reported methods for the preparation of dialkylamides of chlorothioformic acid by reaction of dialkylamides or their hydrochlorides with thiophosgene [1] or the reaction of tetraalkylthiuram disulfides with chlorine [2] have their shortcomings. Reactions according to the first method result in the formation of tetraalkylureas as side products, while the desired compound contains amine hydrochlorides. In the second procedure, side reactions produce sulfur chlorides which contaminate the desired product [3].

Meanwhile, the dimethyl- and diethylamides of chlorothioformic acid, which we prepared by reaction of tetramethyl- and tetraethylthiuram disulfides with SO_2Cl_2, yield upon distillation white crystalline products with sharp boiling and melting points.

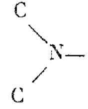
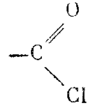


$$R_2N-\overset{S}{\overset{\|}{C}}-SS-\overset{S}{\overset{\|}{C}}-NR_2+SO_2Cl_2\xrightarrow{\text{benzene, }50^\circ}2R_2N-\overset{S}{\overset{\|}{C}}-Cl+2S+SO_2$$

(I), (II)

$R = CH_3$ (I), C_2H_5 (II).

As side products, 3.1% dimethylamide and 1.3% diethylamide of chlorothioformic acid were isolated. The structure of the amides (I) and (II) was confirmed by the ^1H NMR and x-ray structure analysis XSA.

It was established that in the crystal structure the nonhydrogen molecular skeleton of (I) was planar (Fig. 1). The structure of the oxygen analog $(CH_3)_2N-C(O)Cl$ in the gas phase is well known [4]. Within it, the N atom has a planar configuration, but the configuration of the whole molecule is not planar. The dihedral angle between the planar  and  is exactly 26°. The C—Cl bond length in this molecule [1.769(5) Å] is significantly greater than the C—Cl bond length in molecule (I) [1.721 (2) Å]. A value of r(C—Cl) in the range 1.75-1.80 Å is observed in other compounds containing the chlorocarbonyl group, such as chlorocarboxylic anhydrides. This is also observed in the diphenylamide of chloroformic acid [5] and in the mixed *p*-nitrophenylethylamide of chloroformic acid [6], whose structures were examined in the crystalline phase. The specific significance of this value of r(C—Cl) is that it is characteristic for the C_{sp^3}—Cl bond. The C—Cl bond length in vinyl chloride and its derivatives is 1.71-1.72 Å [4], which is also the case for compound (I). Apparently, the lengthening of the C_{sp^2}—Cl bond in systems containing the chlorocarbonyl group may be due to steric effects between O and Cl. This may also be the reason for the increase of the bond angle of O=C—Cl in the dimethylamide of chloroformic acid to 125.9°.

A proton NMR spectrum of (I) taken in DMSO-d_6 shows the two methyl protons resonating as a singlet at δ 2.55 ppm. In benzene, the nonequivalence of the protons of the two methyl groups shows up as two singlets with δ_1 2.50 and δ_2 2.84 ppm.

We have studied the reaction of (I) with KSCN. In contrast to previous findings [3] when the reaction was conducted at 10°C, the final product is not dimethylaminothiocarbonylisothiocyanate, but a further conversion of the initial product to 2-dimethylamino-4-dimethylaminothiocarbonylthio-1,3,5-thiadiazine-6-thione (III). Apparently, the initially formed isothiocyanate undergoes a fast dimerization followed by rearrangement with a 1,3(N→S) migration of the dimethylaminothiocarbonyl group.

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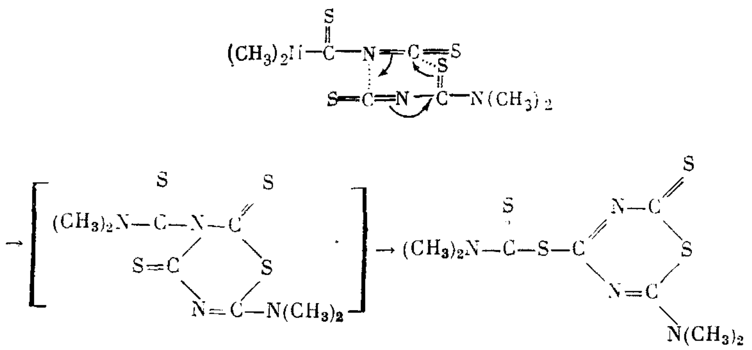

(III)

The structure of (III) was established by XSA, IR and ^1H NMR spectra. IR spectrum (cm^{-1}): 1580 av, 1512 av (ν C=N—C—N), 1448 s (δ_{as} CH_3), 1410 s (δ_s CH_3), 1415 s (ν N—C=S, (I)), 1392 s (ν N—C=S, (II)), 1273 av (ρ CH_3), 1205 av, 1150 av, 1060 av d, 998 av, (ν N—C=S, (III)), δ_s C—N—C, δ_s N—C=S, 860 (ν CSS), 685 w, 627 w, 560 w, 520 w, 470 w, 455 w (δ CSC, C—N—C, N—C—S, N—C—N). The characteristic N=C=S absorption band was not observed in the region 2140-1900 cm^{-1} [7]. The proton chemical shift dependence of the 2- and 4-CH_3 substituents in (III) on the nature of the solvent is manifested in the ^1H NMR as singlets or doublets. The proton signals for the $(CH_3)_2N—C(S)S$ group (δ_2) resonate at a higher field than the protons of the dimethylamino group (δ_1), which are bound directly to the carbon of the heterocyclic ring. ^1H NMR spectrum (δ_1 and δ_2, ppm), in CCl_4: δ_1 3.48 s, δ_2 3.40 s; in $CD_3C{\equiv}N$: δ_1 3.40 s, δ_2 3.20 and 3.00 d; in $C_6H_5—NO_2$: δ_1 3.60 s, δ_2 3.33 and 3.12 d; in CD_3COCD_3: δ_1 3.58 and 3.53 d, δ_2 3.36 and 3.23.

Based on the XSA, the six-membered ring of (III) is practically planar, with a maximum deviation of 0.18 Å observed for the S^1 atom (Fig. 2). The dihedral angle between the planar groups $S^1C^2C^6$ and $C^6N^5C^4N^3C^2$ is 8.6°. The deviations of the exocyclic substituents S^2, S^4, N^2 from the planarity of the ring are not great; 0.16, −0.03, −0.12 Å, respectively. The N^2 atom has a planar bonding configuration, with the sum of the bond angles being 359.9°. The dimethylamino group is situated essentially within the plane of the ring. The deviation of the torsion angle of the $N^2—C^6$ bond from either 0 or 180° does not exceed 6°. The $Me_2N—C(S)—S$ fragment is also planar within the limits of 0.04 Å and forms an angle of 66.9° with the plane of the ring. The $N^2—C^6{=}N^5—C^4{=}N^3—C^2$ chain constitutes a single π-system with an equalization of the bond lengths.

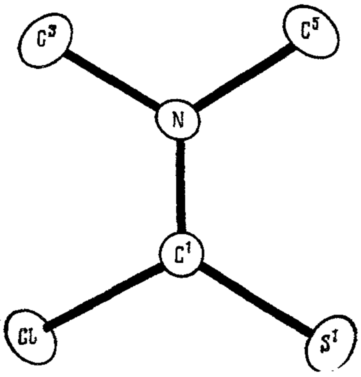

Fig. 1

Fig. 1. Geometry of the dimethylamide of chlorothioformic acid (I).

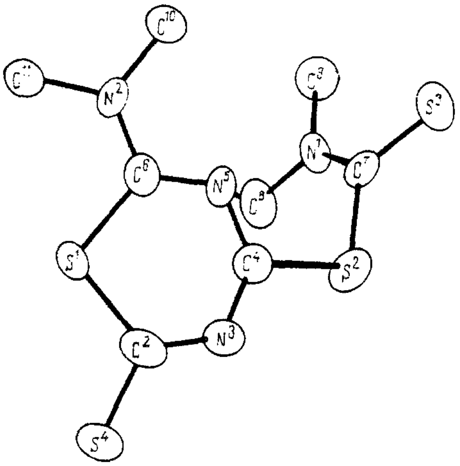

Fig. 2

Fig. 2. Geometry of 2-dimethylamino-4-dimethylaminothiocarbonylthio-1,3,5-thiadiazine-6-thione (III).

EXPERIMENTAL

The ^1H NMR spectra for compound (I) (solvent DMSO-d_6, $Me_3Si(CH_2)_3SO_3Na$ internal standard; solvent benzene, TMS internal standard) and compound (III) (solvent MeCN-d_3, TMS internal standard) were taken on a Varian T-60 (60 MHz) spectrometer. ^1H NMR spectra of compound (III) in CCl_4, acetone-d_6, and nitrobenzene (TMS internal standard) were taken on a Bruker WM-250 (250, 132 MHz) spectrometer. Infrared spectra were recorded on a UR-20 spectrometer. The IR samples were first pulverized in petrolatum oil.

Dimethylamide of Chlorothioformic Acid (I). To a solution of 62 g (0.258 mole) of technical tetramethylthiuram disulfide in 500 ml of anhydrous benzene at 50°C was added dropwise 35 g (0.258 mole) SO_2Cl_2, and the mixture was stirred 6 h at 50°C. The precipitated sulfur was separated and the benzene distilled off. Two successive distillations resulted in the isolation of 1.7 g (3.1%) of the dimethylamide of chlorothioformic acid with bp 52°C (13 hPa). n_D^{20} 1.4540, d_4^{20} 1.1680 (cf. [8]) and 53.2 g (83.2%) (I) with bp 96°C (17 hPa [8]) as a colorless liquid, which quickly crystallized with mp 44°C (cf. [1]). Calculated for C_3H_6ClNS: C, 29.1, H 4.9, N 11.3, S 32.0%. Found: C 29.0, H 4.8, N 11.3, S 31.9%. IR spectrum (ν, cm^{-1}): 1600 av (C—N), 1245 s (C=S), 1530 s (C(S)N) [9].

Diethylamide of Chlorothioformic Acid (II). An analogous reaction of 59.3 g (0.2 mole) tetraethylthiuram disulfide with 27 g (0.2 mole) SO_2Cl_2 in 400 ml anhydrous benzene yielded 0.7 g (1.3%) of the diethylamide of chlorothioformic acid with bp 70°C (13 hPa), n_D^{20} 1.4550, d_4^{20} 1.0941 (cf. [10]). Calculated for $C_5H_{10}ClNO$:* C 44.3, H 7.4, N 10.3, Cl 26.1%. Found: C 44.2, H 7.4, N 10.3, Cl 26.1%. There was also obtained 52.6 g (87%) (II) with mp 46.5°C, bp 111°C (16 hPa) (cf. [11]).

Reaction of (I) with Thiocyanate. To a stirred solution of 2.7 g (0.028 mole) KSCN in 40 ml MeCN at 40°C was added a solution of 3.3 g (0.028 mole) (I) in 10 ml MeCN. After 1 h, the precipitated KCl (2 g, 100%) was filtered off and the filtrate concentrated under reduced pressure (water aspirator) without heating to give a residue which crystallized. Recrystallization from anhydrous acetone yielded 2.6 g (66.5%) 2-dimethylamino-4-dimethylaminothiocarbonylthio-1,3,5-thiadiazine-6-thione (III) as a mixture of yellow threadlike, rhombic, and platelike crystals with mp 125°C. The assigned structure was supported by IR and ^1H NMR spectra. Calculated for $C_8H_{12}N_4S_4$: C 32.8, H 4.1, N 19.2, S 43.8%. Found: C 32.8, H 4.0, N 19.3, S 43.7%. In an analogous reaction, 3.6 g KSCN and 4.6 g (I) in 60 ml anhydrous acetone at 10°C yielded 3.7 g (68%) (III) with mp 125°C.

X-Ray Structural Analysis. Crystals of (I) were monoclinic, at −160°C, a = 6.37(1), b = 6.920(1), c = 6.770(4) Å, β = 111.37(8)°, Z = 2, d_{calc} = 1.48 g/cm³, belonging to the space group $P2_1/m$, and in part situated in the m plane. Crystals of (III) were monoclinic, at 20°C, a = 11.278(2), b = 6.262(2), c = 19.425(3) Å, β = 105.53(1)°, Z = 4, d_{calc} = 1.47 g/cm³, space group $P2_1/c$. The unit-cell parameters and intensities of 699 reflections for (I) and 756 reflections for (III) with F^2 5σ were measured on an automated χ-diffractometer (Enraf-Nonius CAD4) using λMo Kα radiation with a graphite monochromator, with ω/(5/3θ) scans. $\theta \leqslant 30°$ for

TABLE 1. Coordinates of the Nonhydrogen Atoms of (I)

Atom	X	Y	Z	Atom	X	Y	Z
Cl	0.60673(7)	0.250	0.39186(7)	C^1	0.3738(3)	0.250	0.4636(3)
S^1	0.11485(7)	0.250	0.27309(8)	C^3	0.6352(3)	0.250	0.8336(3)
N	0.4083(2)	0.250	0.6680(2)	C^5	0.2169(3)	0.250	0.7390(3)

TABLE 2. Coordinates of the Nonhydrogen Atoms of(III)

Atom	X	Y	Z	Atom	X	Y	Z
S^1	0.5108(2)	0.2414(3)	0.9335(1)	C^2	0.4178(5)	0.034(7)	0.8830(3)
S^2	0.6247(2)	−0.3376(3)	0.8093(1)	C^4	0.5865(5)	−0.134(1)	0.8616(3)
S^3	0.8846(2)	−0.4658(3)	0.8587(1)	C^6	0.6581(5)	0.142(1)	0.9386(3)
S^4	0.2695(5)	0.0671(4)	0.8758(1)	C^7	0.7856(5)	−0.283(1)	0.8170(3)
N^1	0.8104(4)	−0.1098(9)	0.7851(3)	C^8	0.7214(7)	0.043(1)	0.7443(4)
N^2	0.7532(4)	0.2438(9)	0.9818(3)	C^9	0.9357(6)	−0.051(1)	0.7910(4)
N^3	0.4668(4)	−0.1227(9)	0.8543(3)	C^{10}	0.8761(6)	0.159(1)	0.9932(4)
N^5	0.6804(5)	−0.0240(8)	0.9023(3)	C^{11}	0.7396(6)	0.432(1)	1.0220(4)

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*As in Russian original – Editor.

compound (I) and ω/2θ scans, θ ≤ 25° for compound (III). The structure of (I) was solved by the method of Paterson, while structure (III) was solved by the direct method using the MULTAN program. Both structures were refined using the anisotropy approximation. All of the H atoms were located by difference series and were refined at the final stage of the isotopic approximation for only compound (I). The values of the final divergence factors were $R = 0.031$, $R_w = 0.043$ for (I) and $R = 0.036$, $R_w = 0.051$ for (III). All the calculations were performed on a PDP 11/23 computer with the SDP program. Coordinates for the nonhydrogen atoms of (I) and (III) are shown in Tables 1 and 2.

CONCLUSIONS

1. Methods for the preparation of dimethyl- and diethylamides of chlorothioformic acid of greater purity based on the reaction of tetraalkylthiuram disulfides with sulfuryl chloride are presented.

2. Reaction of the dimethylamide of chlorothioformic acid with potassium thiocyanate proceeds through a fast dimerization of the initially produced dimethylaminothiocarbonylisothiocyanate, followed by 1,3 (N→S) migration of the dimethylaminothiocarbonyl group to give 2-dimethylamino-4-dimethylaminothiocarbonylthio-1,3,5-thiadiazine-6-thione.

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