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CHEMISTRY

Reactions of Hexamethylphosphoramide with Sulfur Dichloride with the Ambivalent Participation of Methylene Chloride

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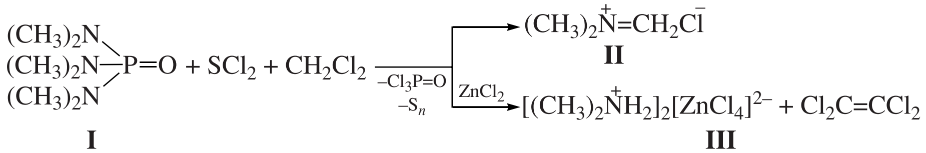
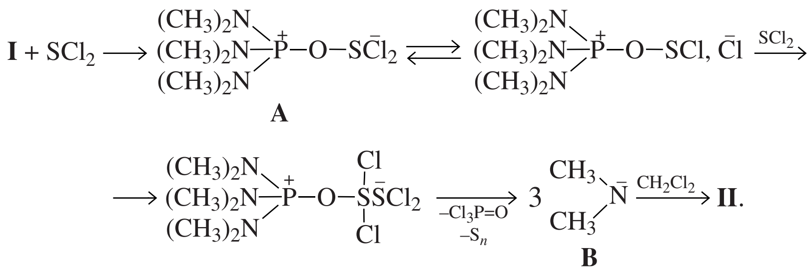
It has been reported in the literature [1] that the reaction of hexamethylphosphoramide (HMPA) (**I**) with hydrogen chloride leads to the protonation of one of the amino groups followed by its elimination as dimethylamine.

We have shown for the first time that the treatment of HMPA with sulfur dichloride or the sulfur dichloride–zinc dichloride system in methylene chloride induces the development of cascade reactions involving methylene chloride, which behaves as the source of methylene fragments (formation of iminium salt **II**) and hydrogen (formation of ammonium salt **III**).



The observed duality in the behavior of HMPA is obviously associated with the different character of nitrogen-containing fragments produced from HMPA when reacted with sulfur dichloride and a sulfur dichloride–zinc dichloride system.

In the reaction of HMPA with sulfur dichloride, the first stage involves the formation of donor–acceptor complex **A** responsible for the generation of ammonium ion **B**, which due to insignificant steric hindrances of the methyl groups in this intermediate and especially of the hydrogen atoms in methylene chloride does not act as a proton harpoon and reacts with methylene chloride as a binucleophile, displacing both geminal chlorine atoms to form iminium salt **II**.



The change in the direction of the HMPA reaction with sulfur dichloride in methylene chloride in the presence of zinc dichloride is apparently caused by the deactivation of the nucleophilic species of the reagent by zinc dichloride:

$$\underset{\textbf{C}}{SCl_2 + ZnCl_2 \rightarrow S^{2+}[ZnCl_4]^{2-}}$$

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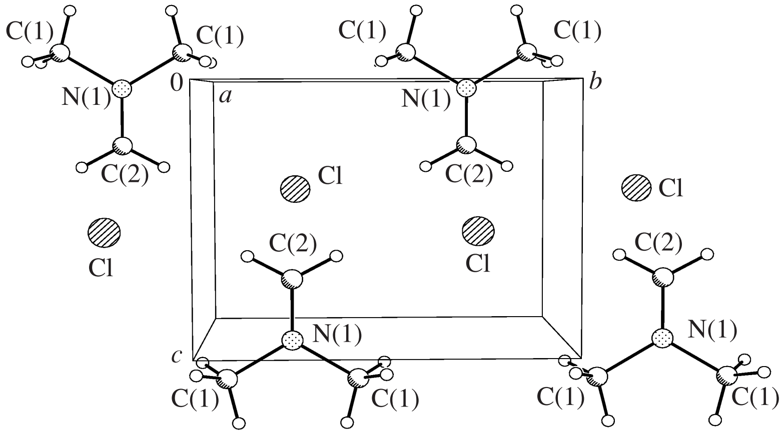
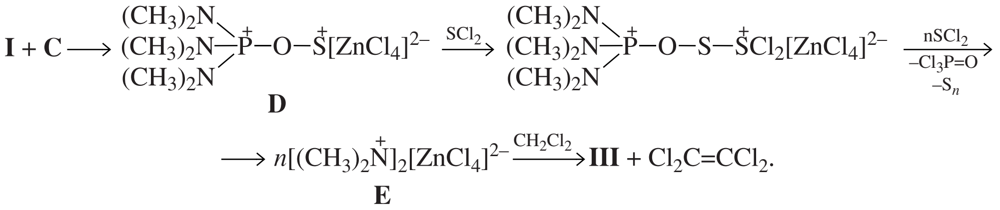


Fig. 1. Crystal structure of dimethyliminium chloride **II**.



$$\mathbf{I} + \mathbf{C} \longrightarrow \underset{\mathbf{D}}{\begin{array}{l}(CH_3)_2N\\(CH_3)_2N{-}\overset{+}{P}{-}O{-}\overset{+}{S}[ZnCl_4]^{2-}\\(CH_3)_2N\end{array}} \xrightarrow{SCl_2} \begin{array}{l}(CH_3)_2N\\(CH_3)_2N{-}\overset{+}{P}{-}O{-}S{-}\overset{+}{S}Cl_2[ZnCl_4]^{2-}\\(CH_3)_2N\end{array} \xrightarrow[\substack{-Cl_3P=O\\ -S_n}]{nSCl_2}$$

$$\longrightarrow \underset{\mathbf{E}}{n[(CH_3)_2\overset{+}{N}]_2[ZnCl_4]^{2-}} \xrightarrow{CH_2Cl_2} \mathbf{III} + Cl_2C{=}CCl_2.$$

Indeed, zinc dichloride eliminates one or two chloride anions in the reagent to convert it into implicit electrophile **C**, which coordinates to HMPA to form a complex reagent **D**, which generates cation **E**, involving methylene chloride into the reaction. However, the *gem* dichloride, as distinct from the first reaction, plays the role of the source of hydride ion and proton to afford dichlorocarbene, which dimerizes to give tetrachloroethylene.

Compound **II** is unstable in air, but relatively stable in a dry nitrogen atmosphere. The crystal and molecular structure of compound **II** (Fig. 1) was confirmed by X-ray diffraction study [2].

The crystal and molecular structure of compound **III** was determined by X-ray diffraction analysis and NMR spectroscopy.

The structural feature of compound **III** is the presence of hydrogen bonds Cl…H (2.33(2)–2.48(2) Å), which are considerably shorter than reduced Cl…H contacts (2.67 Å) [3]. The crystals of compounds **II** and **III** were grown as described in [4] from an acetonitrile solution. Tetrachloroethylene was detected by GLC.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker DPX-200 spectrometer operating at 200 MHz in DMSO-*d*6 solution using TMS as an internal reference. The IR spectra of compounds **II** and **III** were recorded on an UR-20 spectrometer as Nujol mulls. The IR spectra of phosphoryl chloride were obtained on a PerkinElmer-180 spectrophotometer as thin films. The purity of compound **II** was monitored by TLC on Silufol UV-254 plates, Silpearl adsorbent, with hexane–ether (10 : 1) as an eluent and iodine as a developer. GLC analysis was performed on a Tsvet-110 chromatograph (flame ionization detection, 3 m × 3 mm column, 15% Carbowax 6000 on Chromaton N-AW, column thermostat temperature 80°C, injector temperature 150°C, nitrogen carrier gas, flow rate 2 L/h). The X-ray diffraction study of a single crystal of compound **II** was carried out on a Smart APEX2 automated diffractometer (MoK_α radiation, graphite monochromator, ω–θ scan mode). Crystals of compound **II** are orthorhombic, Å: a = 6.0466(4), b = 6.9918(4), c = 5.5606(4), $\alpha = \beta = \gamma$ = 90°, V = 235.08(3) Å^3, Z = 2, space group *Pmmn*. The structure was solved by direct methods and refined by least squares on F^2 in the anisotropic approximation for all non-hydrogen atoms to R = 0.0361 for 549 independent reflections with $I > 2\sigma(I)$ using the SHELXTL V. 5.10 software [5]. The coordinates of the non-hydrogen atoms are presented in Table 1. The structure of molecule **II** is shown in Fig. 1.

The X-ray diffraction study of a single crystal of compound **III** was carried out on a Smart APEX automated diffractometer (MoK_α radiation, graphite monochromator, ω–θ scan mode).

The crystals of compound **III** at 100(2) K are monoclinic, Å: a = 8.3760(5), b = 11.3953(7), c = 13.0976(8), β = 90.091(1)°, V = 1250.13(13) A^3, Z = 4,

Table 1. Non-hydrogen atom coordinates ($Å \cdot 10^{-4}$) for compound **II**

Atom	x	y	z
Cl(1)	2500	7500	5643(1)
C(1)	2500	4269(3)	11148(4)
C(2)	2500	2500	7409(5)
N(1)	2500	2500	9706(5)

space group $P2(1)/n$. The structure was solved by direct methods and refined by least squares on F^2 to R = 0.0195 for 3345 independent reflections with $I > 2\sigma(I)$ using SHELXTL V. 5.10 software complex [6]. The coordinates of non-hydrogen atoms are presented in Table 2. The structure of molecule **III** is shown in Fig. 2.

Reaction of hexamethylphosphoramide with sulfur dichloride. A solution of 1.621 g (15.7 mmol) of SCl_2 in 5 mL of CH_2Cl_2 was added to a solution of 5.6 g (31 mmol) of HMPA in 15 mL of CH_2Cl_2 at –15°C with stirring in nitrogen flow. The mixture was stirred for 1 h. The color disappeared. The solvent was removed under reduced pressure. The residue was recrystallized from acetonitrile. Yield: 3.72 g (90%), white crystals. ^{1}H NMR (DMSO-*d*6, δ, ppm): 2.78 (s, 3H, CH_3), 2.74 (s, 3H, CH_3). IR (ν, cm^{-1}): 1000 (deformation vibrations of CH_3 group), 1200 (stretching vibrations of C–N bonds), 1670 (stretching vibrations of C=N bonds).

Table 2. Non-hydrogen atom coordinates ($Å \cdot 10^{-4}$) for compound **III**

Atom	x	y	z
Zn(1)	1706(1)	1985(1)	4158(1)
Cl(1)	–782(1)	2586(1)	3634(1)
N(1)	2100(1)	57(1)	6656(1)
C(1)	3844(2)	–143(2)	6587(1)
Cl(2)	1886(1)	2652(1)	5794(1)
N(2)	2916(1)	1905(1)	922(1)
C(2)	1498(2)	77(1)	7718(1)
Cl(3)	1828(1)	6(1)	4099(1)
C(3)	1201(2)	2190(2)	782(1)
Cl(4)	3623(1)	2793(1)	3190(1)
C(4)	3223(2)	635(1)	1067(1)

Reaction of hexamethylphosphoramide with sulfur dichloride in the presence of zinc dichloride. The experiment was carried out under conditions that excluded air moisture. A solution of 1.621 g (15.7 mmol) of SCl_2 in 5 mL of CH_2Cl_2 was added dropwise to a stirred mixture of 2.14 g (15.7 mmol) of $ZnCl_2$ in 10 mL of CH_2Cl_2 at –15°C. Then, a solution of 5.6 g (31 mmol) of HMPA in 5 mL of CH_2Cl_2 was added. The mixture was warmed to ambient temperature and stirred for 1 h. The resultant precipitate was filtered off and recrystallized from acetonitrile to give 2.18 g (53%) of compound **III** as a colorless powder, mp 124–126°C (decomp.).

For $C_4H_{16}Cl_4N_2Zn$ anal. calcd. (%): C, 16.05; H, 5.35; Cl, 47.49; N, 9.37; Zn, 21.74.

Found (%): C, 16.32; H, 5.54; Cl, 47.65; N, 9.03; Zn, 21.46.

^{1}H NMR (DMSO-*d*6, δ, ppm): 2.72 (s, 3H, CH_3), 2.66 (s, 3H, CH_3). IR (ν, cm^{-1}): 1000–1050 (deformation vibrations of CH_3 group), 1100 (stretching vibrations of C–N bonds), 3600 (stretching vibrations of N–H bonds).

The solvent from the filtrate was removed under reduced pressure. The residue consists mainly of phosphoryl chloride according to IR spectra. IR (ν, cm^{-1}): 550 (P–Cl), 1295 (P=O).

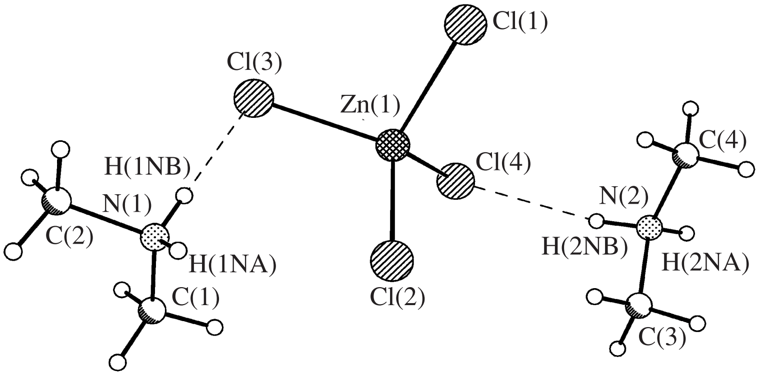


Fig. 2. Crystal structure of dimethylammonium tetrachlorozincate **III**.

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REFERENCES

1. Normant, H., *Angew. Chem.,* 1967, vol. 79, no. 23, pp. 1029–1050.
2. Burg, A.B., *Inorg. Chem.*, 1989, vol. 28, pp. 1295–1300.
3. Zefirov, Yu.V. and Zorkii, P.M., *Usp. Khim.*, 1995, vol. 64, no. 5, p. 446.
4. Stepin, B.D., *Tekhnika laboratornogo eksperimenta v khimii* (Technique of Laboratory Experiment in Chemistry), Moscow: Khimiya, 1999.
5. Sheldrick, G.M., *SHELXTL, Vers. 5.10,* Madison (Wis): Bruker, AXS, 1998.
6. Sheldrick, G.M., *SHELXTL, Vers. 6.10,* Madison (Wis): Bruker, AXS, 2000.