ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 4, pp. 619–620. © Pleiades Publishing, Ltd., 2008.
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SHORT COMMUNICATIONS

Sulfur Dichloride–Hexamethylphosphoric Triamide Complex —A Reagent for Imination of Geminal Dichlorides

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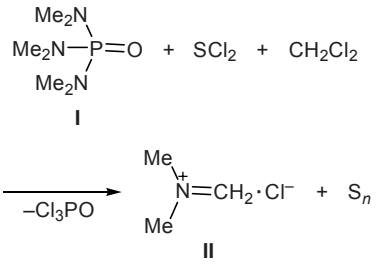
Received August 2, 2007

DOI: 10.1134/S107042800804026X

Normant reported [1] that hydrogen chloride reacts with hexamethylphosphoric triamide (**I**) to give dimethylamine. We were the first to reveal that replacement of hydrogen chloride by sulfur dichloride in methylene chloride gives rise to a new reaction direction involving solvent molecule to produce iminium salt **II** (Scheme 1).

Scheme 1.

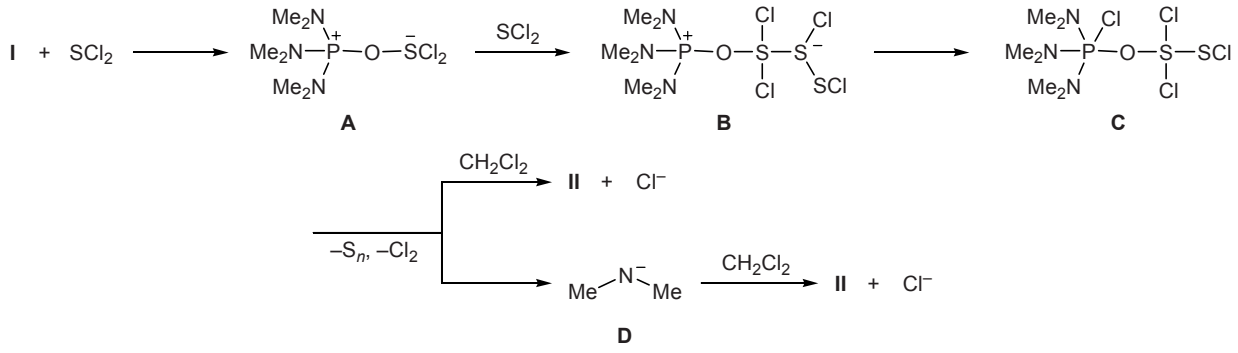


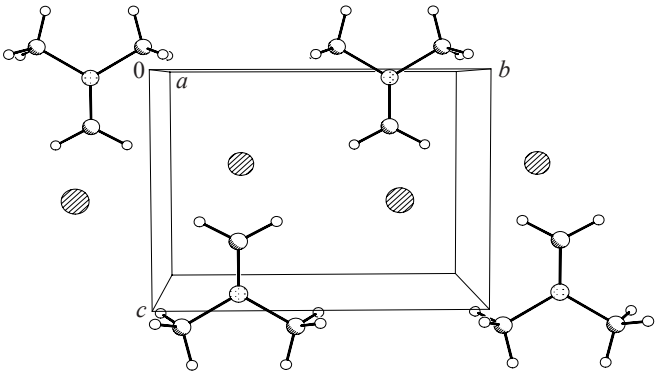
In the first (fast) step, phosphoric triamide **I** with SCl_2 forms donor–acceptor complex **A** in which the sulfur atom becomes a new center for electrophilic attack by the second sulfur dichloride molecule, leading to structure like complex **B**; as a result, oligomeric sulfur chain and molecular chlorine are formed. Chloride ion departing from the negatively charged sulfur atom in complex **B** reacts with the electrophilic phosphorus atom to give intermediate compound **C**. The latter promotes (either directly or with participation of anion **D**) S_N-like reaction of methylene chloride which acts as source of methylene fragment for iminium salt **II** and chloride ion to continue the process, leading finally to the formation of phosphoryl chloride (Scheme 2).

Compound **II** is unstable on exposure to air but is stable under dry nitrogen. The molecular and crystalline structure of iminium salt **II** were determined by X-ray analysis [2]. Orthorhombic crystals, C_3H_8ClN, with the following unit cell parameters [100(2) K]: a = 6.0466(4), b = 6.9918(4), c = 5.5606(4) Å; $\alpha = \beta = \gamma$ = 90°; V = 235.08(3) Å^3; Z = 2; space group P_{mmn}; d_{calc} = 1.322 g/cm^3; μ = 0.627 mm^{-1}; $3.66 \le \theta \le 34.46°$. Total of 3572 reflections were measured, 549 of which were independent (R_{int} = 0.0202); R_1 = 0.0361 [for reflections with $I > 2\sigma(I)$], wR_2 = 0.0990 (for all refelctions).

Thus we have found for the first time that the complex derived from hexamethylphosphoric triamide and sulfur dichloride is an effective iminating agent toward

Scheme 2.





Structure of iminium salt **II** in crystal according to the X-ray diffraction data.

geminal dichloro derivatives and that the iminium salt is formed in nearly quantitative yield.

Crystals of **II** suitable for X-ray analysis were obtained according to the procedure described in [3] from a solution in acetonitrile.

***N*,*N*-Dimethylmethaniminium chloride (II).** A solution of 1.621 g (15.7 mmol) of sulfur dichloride in 5 ml of methylene chloride was added under stirring at –15°C in a stream of nitrogen to a solution of 5.6 g (31 mmol) of hexamethylphosphoric triamide in 15 ml of methylene chloride. The mixture was stirred for 1 h (it turned coloroless), the solvent was distilled off under reduced pressure, and the residue was recrystallized from acetonitrile. Yield 3.72 g (90%), colorless crystals.

The purity of compound **II** was checked by TLC on Silufol UV-254 plates using Silpearl as sorbent and hexane–diethyl ether (10:1) as eluent; the chromatograms were developed by treatment with iodine vapor. The experimental reflection intensities were measured on a Smart APEX2 automatic diffractometer (graphite monochromator, MoK_α irradiation, ω–θ-scanning). The structure was solved by the direct method and was refined by the least-squares procedure with respect to F^2_{hkl} in anisotropic approximation for all non-hydrogen atoms. All calculations were performed with the aid of SHELXTL V. 5.10 software package [4].

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 06-03-32685).

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