[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Phosphorus Chlorothiocyanate and Chlorodiisocyanate. Silicon Methoxythiocyanate

BY HERBERT H. ANDERSON

Pseudo halides previously isolated in this Laboratory included the following substituted derivatives: the silicon methoxyisocyanates,[1] $Si(OCH_3)_3(NCO)$, $Si(OCH_3)_2(NCO)_2$, and $Si(OCH_3)(NCO)_3$; silicon trichlorothiocyanate,[2] $SiCl_3(SCN)$; silicon chloroisocyanates,[3] $SiCl_3(NCO)$, $SiCl_2(NCO)_2$, and $SiCl(NCO)_3$; phosphoryl dichlorothiocyanate,[2] $POCl_2(SCN)$; phosphorus dichloroisocyanate,[2] $PCl_2(NCO)$, and indication[2] of a second mixed halide, supposedly phosphorus chlorodiisocyanate, $PCl(NCO)_2$.

The existence of silicon trichlorothiocyanate and phosphoryl dichlorothiocyanate prompted an effort to prepare phosphorus dichlorothiocyanate, PCl_2SCN, expected to be far less stable than silicon trichlorothiocyanate, and somewhat less stable than phosphoryl dichlorothiocyanate. Distillation at 50-mm. pressure yielded pure phosphorus dichlorothiocyanate as described later. At least silicon trimethoxythiocyanate was to be expected, in its own series of possible compounds, since silicon trichlorothiocyanate and all the silicon methoxyisocyanates had been successfully prepared. As shown below, it was isolated in a state of adequate purity, but the di- and mono-methoxy compounds were not obtained.

Preparation of the three new compounds involves difficulties beyond the average and should be undertaken only after some experience with closely related compounds. The isomerization or polymerization of phosphorus trithiocyanate into a black mass is especially troublesome. Methods described below have given moderate yields of desired intermediates in every run made.

Silicon Trimethoxythiocyanate.—Thirty-two g. (1 mole) of absolute methanol was added gradually to 124 g. (0.48 mole) of liquid silicon tetrathiocyanate at about 145°; the alcohol diffused downward through a capillary into the thiocyanate, with vigorous reaction. Distillation of the reaction products, whether at 760 mm. and 171° or at 70 mm. and 110°, yielded only one intermediate, silicon trimethoxythiocyanate, about 30 g. in amount. The crude product was redistilled and the middle fraction, taken for measurements, boiled at 171–172° uncor.

Analysis for thiocyanate content was made through decomposition in alcohol and subsequent titration with standard silver nitrate using ferric nitrate as indicator. Calcd. for $Si(OCH_3)_3SCN$: 32.41% SCN; mol. wt., (Dumas), 179.2. Found: SCN, 32.4, 32.4; mol. wt., 185, 189. Boiling point at 760 mm., found 170.5°. Density was by 2-ml. bulb with calibrated capillary inlet, accurate to 1 or 2 parts per thousand, 1.134 at 20°, 1.119 at 30°; index of refraction in white light (Abbe refractometer), 1.4426 at 20°; vapor pressure, from 760 and 70 mm. points only, approximately $\log p = 9.48821 - 2931/T$; λ, heat of vaporization, approximately 13,400 cal.; λ/T = 30.2 cal./°, roughly.

Phosphorus Dichlorothiocyanate.—The typical preparation consisted of very gradual addition of 165 g. of dry silver thiocyanate to 127 ml. of phosphorus trichloride in the ratio SCN/4.4 Cl, with continuous agitation. Thereupon, the mixture was heated on a steam-bath an hour in the presence of 5 g. of adsorbent charcoal, in an attempt to adsorb the yet unidentified "catalyst" for isomerization of phosphorus trithiocyanate. It is to be noted that this compound when pure can be distilled many times without any formation of a shiny black solid.

After filtration, in the hope of avoiding impurities, washing of the silver salt was omitted. Three types of procedures for isolating phosphorus dichlorothiocyanate by distillation were tried. Removal of phosphorus trichloride by distillation at 760 mm., in the absence of metal, and subsequent distillation at 73 mm. and about 90° yielded 15 g. or 0.09 mole of crude phosphorus dichlorothiocyanate, and also 15 g. of liquid phosphorus trithiocyanate, with about 15 g. lost as black polymeric trithiocyanate. A run using a copper spiral and conditions otherwise similar to the first method gave only 0.04 mole of the dichloro compound, $PCl_2(SCN)$, but all the trithiocyanate was lost as a black solid; this suggests that copper may be a decomposition catalyst. The last and best method consisted of distilling first at 300 mm. in the absence of metal, to remove phosphorus trichloride, and then distilling at 78–82° under a pressure of 48 mm.; this method gave 0.15 mole of phosphorus dichlorothiocyanate and 0.08 mole of volatile trithiocyanate, perhaps 60% of the latter compound going into a sticky black mass. At best 1 mole of silver thiocyanate gave only 0.15 mole of phosphorus dichlorothiocyanate. Use of three times as much phosphorus trichloride, washing the final silver salt, and avoidance of "polymerization" would probably double the yield under ideal circumstances.

Twenty ml. of crude phosphorus dichlorothiocyanate was redistilled once, with rejection of first and last quarters; the new product was redistilled with rejection of the first and last fifths. Six ml. of pure product boiled at 81–82° at 45 mm. Equipment used was similar in general nature (6-mm. tubing, no spiral, high reflux ratio, 30 cm. height) to that used by Rose.[4] A distillation period of one hour only limited redistribution of phosphorus dichlorothiocyanate to 1% or less.

Physical measurements were made at once; Table I below lists the chief properties. The liquid cools to a glass in liquid air, but is converted by stirring into crystals yielding a sharp m. p. In this respect silicon trichlorothiocyanate, phosphoryl dichlorothiocyanate, phosphorus dichloroisocyanate and phosphorus chlorodiisocyanate all behave similarly. The respective densities of phosphorus dichlorothiocyanate and chlorodiisocyanate were measured in a special 1 ml. micropycnometer, wherein the volume could be read to one part in two thousand, or better. The b. p. was approximately 148° but the accuracy of measurement was somewhat limited by the considerable speed of rearrangement.

Analysis.—% SCN by electrometric titration, found 36.2, 36.7%; calcd. 36.30% SCN for phosphorus dichlorothiocyanate. The chloride end-point was indistinct in each of the two titrations, presumably because of the presence of phosphorous acid. Equivalent wt. of compound by titration with silver nitrate using chromate indicator was found to be 53.4 and 53.5 g. per gram equivalent of halogen, while one-third of the formula weight PCl_2SCN is 53.34 g. Molecular weight (Dumas), calcd. 160.0; found, 167. All these data tend to confirm the formula PCl_2SCN. Hydrolysis of $PCl_2(SCN)$ is rapid, like that of

---

(1) Forbes and Anderson, THIS JOURNAL, **66**, 1703 (1944).

(2) Anderson, *ibid.*, **67**, 223 (1945).

(3) Anderson, *ibid.*, **66**, 934 (1944).

(4) A. Rose, *Ind. Eng. Chem.*, **28**, 1210 (1936).

phosphorus trichloride. Vapor pressure equation from 760 mm. point and five points in the range 30–54 mm., approximately $\log p = 9.42681 - 2756.6/T$; λ, heat of vap., approximately 12,600 cal.; $\lambda/T_B = \sim 29.9$ cal./°.

Disproportionation.—The reaction $3PCl_2(SCN) \rightarrow 2PCl_3 + P(SCN)_3$ was too rapid at 148° to permit isolation of a pure product. An experiment in a small tube for ten minutes indicated the order of magnitude of decomposition to be roughly 1% per minute at this temperature.

Phosphorus Chlorodi(iso)cyanate.—In new preparations each unit involved addition of 200 g. of silver isocyanate in small portions to a mixture of 90 ml. of phosphorus trichloride and 125 ml. of pure benzene, over a period of one hour. Each unit of preparation yielded about 0.033 mole of phosphorus dichloroisocyanate and about 0.056 mole of phosphorus chlorodiisocyanate, both distilled under 167 mm. pressure. Crudes from four units were combined and distilled a second and then, finally, a third time yielding 4 ml. of pure phosphorus chlorodiisocyanate boiling at 67–68° at 50 mm. free from any appreciable amount of either the lower boiling phosphorus dichloroisocyanate or the higher boiling phosphorus isocyanate. The physical measurements listed in Table I were made immediately after the final distillation. Stirring converted the glass first formed upon cooling with Dry Ice and alcohol into crystals melting rather sharply at −50°. Vapor pressure equation, from 760, 167, and 50 mm. values, approximately $\log p = 8.87981 - 2445.2/T$; $\lambda = 11{,}200$ cal.; $\lambda/T = 27.4$ cal./°. Mol. wt. (Dumas), calcd. for $PCl(NCO)_2$, 150.5; found 148. Per cent. Cl by titration with silver nitrate and a chromate indicator, found 23.4, 23.7%; calcd. for $PCl(NCO)_2$, 23.58% Cl. Hydrolysis was rapid.

TABLE I

PROPERTIES OF THE NEW COMPOUNDS

Compound	B. p., °C.	M. p., °C.	Density$^{30}{}_4$
$Si(OCH_3)_3SCN$	170.5 ± 1	......	1.134, 1.119 at 30°
$PCl_2(SCN)$	148 ± 1	−76 ± 2	1.546, 1.539 at 25°
$PCl(NCO)_2$	134.6 ± 1	−50 ± 2	1.505, 1.497 at 25°

Disproportionation.—In a previous one-hour distillation at 760 mm. about 80% of the phosphorus chlorodiisocyanate, b. p. 135°, rearranged into dichloroisocyanate, b. p. 104.4°, and triisocyanate, b. p. 169.3°, according to the equation $2PCl(NCO)_2 \rightleftarrows PCl_2(NCO) + P(NCO)_3$. When phosphorus chlorodiisocyanate was refluxed in a small tube for three minutes, during which some escaped, the residue was found, through rapid distillation, to contain about 3% of phosphorus triisocyanate. When these rates are used to estimate rearrangement in one hour at 67.5° and 50 mm., a value of about 1% for phosphorus chlorodiisocyanate is obtained. Rearrangement of phosphorus dichlorothiocyanate, also, was quite severe during distillation at 760 mm. The products were phosphorus trichloride and trithiocyanate.

Discussion

1. Seven phosphorus mixed halides now known include three rather stable members, phosphorus difluorochloride,[5] fluorodichloride,[5] and dichloroisocyanate.[2] The stability of phosphorus fluorodibromide[6] is probably intermediate, approaching that of these first three compounds. Definitely less stable are phosphorus chlorodiisocyanate, dichlorothiocyanate and difluorobromide.[6] Phosphorus dichloroisocyanate is more stable than the analogous dichlorothiocyanate as could be expected.[2] The relatively low stability of phosphorus chlorodiisocyanate would scarcely have been predicted; its rate of rearrangement is roughly 100 times as great as that of the dichloro compound at the same temperature.

2. Only silicon trimethoxythiocyanate exists in its series, though the three possible methoxy isocyanates have been obtained in stable form. Actually, samples of silicon trimethoxythiocyanate and trimethoxyisocyanate (previously prepared) are decomposing very slowly into solids, at room temperature; in a few years micro-investigation should be possible.

3. Classification of compounds described above as thiocyanates rather than as isothiocyanates is being maintained provisionally in keeping with the rather positive assertions made by Reynolds regarding silicon thiocyanate.[7] Dixon[8] first observed the transformation of phosphorus thiocyanate into a black solid.. This issue of structure is still unsettled, and may presently be decided by examination of molar refractions of the thiocyanate group; preliminary calculations have been made, but these rest upon two compounds only. Further synthesis and measurements may decide this question.

Other work is in progress including study of the three mixed silicon isocyanate thiocyanates, all apparently produced by thermal redistribution of silicon tetraisocyanate with silicon tetrathiocyanate. The author acknowledges many helpful suggestions from Professor George S. Forbes, of this Laboratory.

Summary

1. Reaction of methanol with silicon tetrathiocyanate, $Si(SCN)_4$, has given only one stable new compound, silicon trimethoxythiocyanate, $Si(OCH_3)_3SCN$, b. p. 170.5°.

2. Action of the appropriate silver salt on a large excess of PCl_3 has yielded phosphorus dichlorothiocyanate, $PCl_2(SCN)$, b. p. 148°, and phosphorus chlorodiisocyanate, $PCl(NCO)_2$, b. p. 134.6°, both of which have been obtained in pure states. Distillation at 50 mm. pressure is necessary to avoid decomposition. The related dichloroisocyanate, $PCl_2(NCO)$, has been described previously.

3. The chief physical properties of the new compounds have been determined; observations of rearrangement of halide groups and a comparison of stabilities have been made. Further investigation of compounds containing the thiocyanate group should establish its configuration (normal or iso).

CAMBRIDGE, MASS. RECEIVED JULY 20, 1945

---

[5] Booth and Bozarth, THIS JOURNAL, **61**, 2927 (1939).

[6] Booth and Frary, *ibid.*, **61**, 2934 (1939).

[7] Reynolds, *J. Chem. Soc.*, **89**, 397 (1906).

[8] Dixon, *ibid.*, **79**, 541 (1901).