and 63.7% of acetophenone. The fluorine analysis indicates 45% of *p*-fluoroacetophenone and 55% of acetophenone. We consider the carbon analysis to be more accurate than the fluorine analysis, and calculated yields based on the results of the carbon analysis are given in Table I.

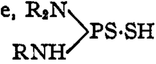
In each reaction a copious amine fraction was also obtained, but no attempt was made to separate the components. Sulfonation derivatives were also formed in some of the reactions.

LAWRENCE, KANSAS RECEIVED AUGUST 6, 1951

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

The Reaction of *s*-Aliphatic Amines with Phosphorus Pentasulfide; Thiophosphoric Amides. II

BY GENE WISE[1] AND HERMAN P. LANKELMA

s-Aliphatic amines, R_2NH, react with phosphorus pentasulfide to give thiophosphoric amides. Depending upon reaction conditions a monamide, $R_2N{\cdot}PS(SH)_2$, a mixed diamide,  $\begin{matrix}R_2N\\RNH\end{matrix}\!\!>\!PS{\cdot}SH$, or a triamide $(RNH)_3PS$ is obtained. By further reaction with the amine, the monamide is easily converted to the diamide and the latter to the triamide. Amides of the above types were prepared using di-*n*-propyl-, di-*n*-butyl-, di-*n*-amyl- and dibenzylamines. No diamides $(R_2N)_2PS(SH)$ or triamides $(R_2N)_3PS$ were obtained.

Previous work in this Laboratory[2] has shown that phosphorus pentasulfide forms diamides $(RNH_2)PS{\cdot}SH$, with primary aromatic amines and triamides $(RNH)_3PS$ with both primary aliphatic and aromatic amines. Attempts to prepare a monamide $(RHN)PS{\cdot}(SH)_2$, from aniline were unsuccessful. Attempts to prepare triamides, $(R_2N)_3PS$, from *s*-aliphatic amines and phosphorus pentasulfide gave oils which were not obtained in analytical purity. Michaelis[3] reported the preparation of the triamide, N,N′,N″-hexaethylthiophosphoramide′ $[C_2H_5)_2N]_3PS$, from N-diethyl amidodichlorothiophosphate $(C_2H_5)_2N]_3P$, and sulfur. It was described as an oil which could not be distilled even *in vacuo*. It was identified by analysis for nitrogen which gave only fair agreement with the calculated value.

The present work is a further study of the reaction of *s*-aliphatic amines with phosphorus pentasulfide. The amines employed were di-*n*-propyl, di-*n*-butyl, di-*n*-amyl and dibenzyl. Parallel results were obtained with each. Di-*n*-butylamine will be used for discussion.

Buck, Bartleson and Lankelma[2] obtained diamides, $(RHN)_2PSSH$, by the action of aniline and *o*-chloroaniline with phosphorus pentasulfide in molar ratios of 4:1. The reaction was carried out at a temperature of about 30° in a diluent such as toluene. The reaction occurred rapidly, with a copious evolution of hydrogen sulfide. With dibutylamine, under the same conditions, we obtained a yellow insoluble product, but no hydrogen sulfide was released. Since the filtrate contained appreciable amounts of unreacted amine, the reaction was repeated, using two molar quantities of amine. The reaction proceeded as before, and the yield from a given amount of phosphorus pentasulfide was the same. The product was water insoluble and alkali soluble. Upon exposure to air, it hydrolyzed quite rapidly, releasing hydrogen sulfide but it could be kept in a desiccator over phosphorus pentoxide. Analysis agreed with the formula for the monamide.

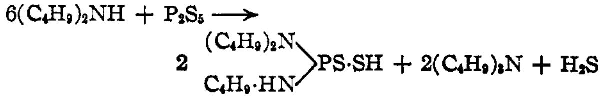
The formation of the monamide could occur by the reaction

$$2(C_4H_9)_2NH + P_2S_5 \longrightarrow (C_4H_9)_2NPS{\cdot}(SH)_2 + (C_4H_9)_2NPS_3$$

The identity of the second product of this reaction could not be established. The filtrate upon removal of the solvent yielded a viscous sticky resin which could not be purified.

By heating six moles of amine with one mole of phosphorus pentasulfide at temperatures of 150–180° triamides, $(RHN)_3PS$, have been obtained from both aliphatic and aromatic primary amines. The cyclic *s*-amine, tetrahydroquinoline also gave a triamide, $(C_9H_{10}N)_3PS$.[2]

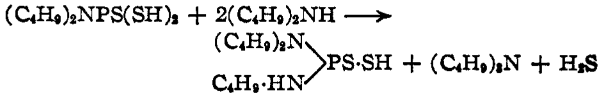
With *s*-aliphatic amines, such as dibutylamine, as previously stated, oils were obtained which were not identified, since attempts to purify them were unsuccessful. We found similarly that heating the amine with phosphorus pentasulfide using from one to eight moles of amine to one mole of phosphorus pentasulfide gave only brittle resins or sticky viscous oils. With higher molar ratios of amine, 12 to 15/1, however, a white crystalline solid separated at about 150°. This product was insoluble in water, but soluble in dilute sodium hydroxide solution. It was much more stable in air than the monamide and could be crystallized from methyl alcohol. The product was identified as a mixed diamide by analysis. The over-all reaction may be represented by the equation



$$6(C_4H_9)_2NH + P_2S_5 \longrightarrow 2\begin{matrix}(C_4H_9)_2N\\C_4H_9{\cdot}HN\end{matrix}\!\!>\!PS{\cdot}SH + 2(C_4H_9)_3N + H_2S$$

The tributylamine was not identified here but was shown to be present in the next stage of the reaction, the formation of the triamide.

The same mixed diamide was obtained in good yield by heating the monamide with an excess of amine for about an hour at 160°.



$$(C_4H_9)_2NPS(SH)_2 + 2(C_4H_9)_2NH \longrightarrow \begin{matrix}(C_4H_9)_2N\\C_4H_9{\cdot}HN\end{matrix}\!\!>\!PS{\cdot}SH + (C_4H_9)_3N + H_2S$$

When the reaction mixture just described was

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[1] Standard Oil Co. (Ohio) Fellow in Chemistry, Western Reserve University, 1949–1950.

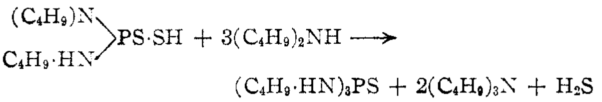
[2] A. C. Buck, J. D. Bartleson and H. P. Lankelma, THIS JOURNAL, **70**, 744 (1948).

[3] A. Michaelis, *Ann.*, **326**, 129 (1903).

heated further at the boiling point of the amine, the diamide which precipitated during the first few hours slowly dissolved with evolution of hydrogen sulfide and after three to five days, a clear solution resulted. Removal of the excess amine left a viscous oily liquid, which upon purification gave a crystalline solid which was identified as the triamide of *n*-butylamine. The over-all reaction may be represented by the equation

$$12(C_4H_9)_2NH + P_2S_5 \longrightarrow 2(C_4H_9NH)_3PS + 6(C_4H_9)_3N + 3H_2S$$

or from the intermediate diamide.



$$\begin{matrix}(C_4H_9)N\\C_4H_9{\cdot}HN\end{matrix}\!\!>PS{\cdot}SH + 3(C_4H_9)_2NH \longrightarrow (C_4H_9{\cdot}HN)_3PS + 2(C_4H_9)_3N + H_2S$$

Tributylamine was separated from the reaction mixture in yields of the same order as the triamide. The triamide is insoluble in water and in sodium hydroxide solution and is very stable to hydrolysis.

Experimental

Materials.—The phosphorus pentasulfide was a commercial grade purified by extraction with carbon bisulfide in a soxhlet extractor. It melted at 277–283°. The amines were purified by distillation.

The Monamides. N-Dialkylamidothiophosphoric Acids, $(R_2N)PS.(SH)_2$.—The preparation of N-di-*n*-butylamidothiophosphoric acid is illustrative. Fifteen grams (0.067 mole) of finely divided phosphorus pentasulfide was mixed with 120 ml. of benzene in a dry 300-ml. three-neck flask, equipped with a mercury seal stirrer, dropping funnel and reflux condenser fitted with a drying tube. The mixture was cooled to 5° in an ice-bath and 17.5 g. (0.14 mole) of di-*n*-butylamine was added drop-wise with stirring. The flask was then placed in a water-bath at 30° for three hours although the formation of the solid monamide appeared to be complete after the first hour. There was no evolution of hydrogen sulfide. The reaction mixture was filtered and the filtrate washed three times with petroleum ether and dried over phosphoric anhydride in a vacuum desiccator; yield 15.9 g.; m.p. 189–192°. The product was insoluble in ether and in hydrocarbon solvents. It dissolved in alcohol and in chloroform but with the release of hydrogen sulfide. Having found purification by recrystallization unsatisfactory, the monamide was continuously extracted with carbon bisulfide for two days in a soxhlet extractor. After drying in a vacuum desiccator for four days, the monamide melted reversibly at 191–193° in a sealed capillary tube. When exposed to air, the monamide hydrolyzed, releasing hydrogen sulfide. It was insoluble in water and soluble in dilute sodium hydroxide solution but could not be precipitated from the alkaline solution unchanged. Solutions of silver nitrate, barium chloride and nickel chloride added to portions of the monamide dissolved in alcohol precipitated insoluble salts. These salts were insoluble in water and organic solvents.

$(C_4H_9)_2NPS(SH)_2$, m.p. 191–193°. *Anal.* Calcd. for $C_8H_{20}NPS_3$: C, 37.33; H, 7.83; N, 5.44; P, 12.04. Found: C, 37.94; H, 8.08; N, 5.52; P, 12.17.

$(C_3H_7)_2NPS(SH)_2$, m.p. 167–170°. *Anal.* Calcd. for $C_6H_{16}NPS_3$: P, 13.82. Found: P, 13.52.

$(C_5H_{11})_2NPS(SH)_2$, m.p. 151–154°. *Anal.* Calcd. for $C_{10}H_{24}NPS_3$: P, 10.85. Found: P, 11.00.

The Diamides: N,N′-Trialkyldiamidothiophosphoric Acids, $\begin{matrix}R_2N\\RHN\end{matrix}\!\!>PS(SH)$.—The preparation of N-di-*n*-butyl-N′-*n*-butyldiamidothiophosphoric acid is illustrative. Fifteen grams (0.067 mole) of phosphorus pentasulfide was added to 130 g. (1 mole) of di-*n*-butylamine in a 300-ml. three-neck flask equipped with mercury seal stirrer, reflux condenser and thermometer. There was an immediate exothermic reaction. Upon heating, a clear homogeneous solution was obtained at 80–90°, and at 145° a white solid began to separate. The heating was continued at 160° for four hours, during which time large quantities of the insoluble product formed. This was accompanied by a copious evolution of hydrogen sulfide. The reaction mixture was cooled and filtered by suction. The filtrate was washed with petroleum ether and dried. Nineteen grams of product, m.p. 208–213°, was obtained. Upon recrystallization from methyl alcohol, it melted at 215–217°. The product was insoluble in water but dissolved rapidly in dilute sodium hydroxide solution. It was much more stable in air than the monamide. Solutions of silver nitrate, barium chloride and nickel chloride added to portions of the compound dissolved in methyl alcohol precipitated insoluble salts. These salts were insoluble in water and organic solvents.

The same diamide was obtained by the further action of di-*n*-butylamine on the monamide. Seven and four-tenths grams (0.03 mole) of the monamide, N-di-*n*-butylamidothiophosphoric acid and 38 g. (0.29 mole) of di-*n*-butylamine were heated together at 160° for one hour. The insoluble diamide separated from the reaction mixture during the first half-hour. Four grams of diamide, m.p. 208–213°, was obtained. Upon crystallization from methyl alcohol it melted at 211–213°. The melting point was not depressed when mixed with a portion of diamide, m.p. 215–217°, prepared directly from phosphorus pentasulfide and di-*n*-butylamine.

$(C_4H_9)_2NPS(SH)NHC_4H_9$, m.p. 215–217°. *Anal.* Calcd. for $C_{12}H_{29}N_2PS_2$: C, 48.61; H, 9.86; N, 9.45; P, 10.45; S, 21.63. Found: C, 48.68; H, 9.85; N, 9.49; P, 10.57; S, 21.94.

$(C_3H_7)_2NPS(SH)NHC_3H_7$, m.p. 194–196°. *Anal.* Calcd. for $C_9H_{23}N_2PS_2$: P, 12.18; S, 25.21. Found: P, 12.01; S, 25.56.

$(C_5H_{11})_2NPS(SH)NHC_5H_{11}$, m.p. 212–214°. *Anal.* Calcd. for $C_{15}H_{35}N_2PS_2$: P, 9.15; S, 18.94. Found: P, 9.10; S, 19.48.

The Triamides; N,N′,N″-Trialkylthiophosphoramides, $(RHN)_3PS$.—Here also the reaction of di-*n*-butylamine is illustrative. The apparatus was the same as that described in the previous paragraph. Twenty-three grams (0.10 mole) of phosphorus pentasulfide and 179 g. (1.39 moles) of di-*n*-butylamine were heated together at 160–170° for four days. The insoluble diamide which formed early in the reaction and was present in suspension for three days, dissolved completely on the fourth day to give a clear solution. There was evolution of hydrogen sulfide throughout the reaction period. The mixture was steam distilled to remove unreacted amine and volatile reaction products. The residue was dissolved in ether and washed successively with 5% hydrochloric acid, 3% sodium hydroxide solution and water. The ether solution was then dried over anhydrous sodium carbonate, and the ether removed on a steam-bath. The residue, a viscous yellow oil, weighed 31.8 g. It was dissolved in 200 ml. of petroleum ether and boiled with Norit decolorizing carbon, filtered hot and cooled to −60° in a Dry Ice chest. At the low temperature, 10.2 g. of crystalline solid was obtained. Upon recrystallizing twice more from petroleum ether at 0°, the product melted at 54°. It was insoluble in water, and dilute sodium hydroxide, and was very stable toward hydrolysis. Analysis for the elements agreed with the formula for N,N′,N″-tri-*n*-butylthiophosphoramide, $(C_4H_9NH)_3PS$.

The presence of tributylamine as a product of this reaction was shown as follows: The reaction product of 101.4 g. (0.78 mole) of di-*n*-butylamine and 12.4 g. (0.056 mole) of phosphorus pentasulfide was distilled. The distillate, 100 ml., was dissolved in 6 *N* sulfuric acid and a portion distilled off. The distillate gave 3 g. of an oil which appeared to be a sulfide but was not identified. The acid solution was then extracted with ether and made alkaline with sodium hydroxide solution. The amines which separated were dried over potassium hydroxide. Distillation of 40 g. gave a fraction of 8 g. boiling at 210–214°. This was identified as tributylamine by converting it to the quaternary ammonium salt with methyl iodide; m.p. 183°. The addition of the quaternary ammonium salt prepared from tributylamine, to this substance did not lower its melting point.

The structure of the triamide was confirmed by preparing it from mono-*n*-butylamine and thiophosphoryl chloride. Twenty-five grams (0.34 mole) of *n*-butylamine dissolved in 50 ml. of dry ether was cooled to 5° in an ice-bath, and 9.6 g. (0.57 mole) of thiophosphoryl chloride dissolved in 30 ml. of dry ether was added dropwise with stirring. The mixture was then refluxed for three hours. The butylamine hydrochloride was filtered off, and the triamide recovered from the ether solution and purified as described in the previous paragraph. Twelve and four-tenths grams of a pale yellow oil was obtained from which 9.4 g. of crystalline material, m.p. 52–53° was obtained. Recrystallization from petroleum ether raised the melting point to 54°. The addition of this amide to the product obtained from dibutylamine and phosphorus pentasulfide did not depress its melting point.

$(C_4H_9NH)_3PS$, m.p. 54°. *Anal.* Calcd. for $C_{12}H_{30}N_3PS$: C, 51.58; H, 10.82; N, 15.04; P, 11.09. Found: C, 51.63; H, 10.92; N, 14.95; P, 11.72.

$(C_6H_5CH_2NH)_3PS$, m.p. 122–123°. The addition of the triamide, m.p. 123–125°, prepared from benzylamine and phosphorus pentasulfide,[2] to this substance did not lower its melting point.

CLEVELAND, OHIO RECEIVED JULY 9, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Preparation of Triphenyltin-lithium and Some of Its Reactions

BY HENRY GILMAN AND SANDERS D. ROSENBERG

The preparation of triphenyltin-lithium from stannous chloride and phenyllithium is described together with an account of some of its chemical properties. Tetraphenyltin, triphenylbenzyltin, triphenylethyltin, hexaphenylditin and triphenylsilyl-triphenyltin have been prepared by the reaction of triphenyltin-lithium with appropriate halides. In addition, some other reactions are described.

Investigations in this Laboratory have shown[1] that lead dichloride reacts with three equivalents of phenyllithium in the cold to form triphenyllead-lithium, and that treatment of this intermediate with appropriate halides gives organolead derivatives of the type $(C_6H_5)_3PbR$ in good yields. Similar reactions have been carried out with dihalides of other Group IV-B elements. The results obtained from the reaction of phenyllithium with germanium diiodide, GeI_2, will be reported later.[2]

In a recent article[3] Wittig and co-workers reported that triphenyltin-lithium has been prepared by treating diphenyltin with one equivalent of phenyllithium. It has been found in this Laboratory that triphenyltin-lithium can be prepared directly by treating finely ground, anhydrous stannous chloride[4] with three equivalents of phenyllithium in the cold, thereby eliminating the preparation of diphenyltin. A series of color changes takes place as the addition of the phenyllithium progresses. When the first equivalent of phenyllithium has been added the reaction mixture is orange in color; the addition of the second equivalent changes the color to deep red[5]; the third equivalent turns the color to light tan.

Triphenyltin-lithium has been treated with a series of halides in order to form some unsymmetrical organotin compounds of the type $(C_6H_5)_3SnR$, and to explore the procedure for the introduction of water-solubilizing groups. The path of the reactions has been postulated as

$$SnCl_2 + 2C_6H_5Li \longrightarrow (C_6H_5)_2Sn + 2LiCl \quad (1)$$

$$(C_6H_5)_2Sn + C_6H_5Li \longrightarrow (C_6H_5)_3SnLi \quad (2)$$

$$(C_6H_5)_3SnLi + RX \longrightarrow (C_6H_5)_3SnR + LiX \quad (3)$$

In the reactions of triphenyltin-lithium with benzyl chloride and ethyl iodide a considerable amount (60.0 and 26.9%, respectively) of tetraphenyltin was isolated; reactions with iodobenzene, triphenyltin chloride and triphenylchlorosilane yielded only the expected products in good yields.

It has been shown[1] that equation (2) applied to the lead series

$$(C_6H_5)_2Pb + C_6H_5Li \rightleftharpoons (C_6H_5)_3PbLi \quad (4)$$

represents an equilibrium system with the equilibrium displaced 80% toward the triphenyllead-lithium. It has not yet been rigorously established whether triphenyltin-lithium is involved in a related equilibrium system. Carbonation of triphenyltin-lithium by passing carbon dioxide gas over the surface of the reaction mixture for five hours yielded no benzoic acid or addition products of benzoic acid. Addition of benzophenone to triphenyltin-lithium yielded no detectable amounts of triphenylcarbinol and led only to recovery of benzophenone. Color Test I[6] remains negative until slightly more than three equivalents of phenyllithium have been added.[7]

Further experiments designed to explain the formation of the tetraphenyltin and elucidate the exact nature of the triphenyltin-lithium intermediate are now being carried out.

Experimental

Triphenyltin-lithium.—To a well-stirred suspension of 8.54 g. (0.045 mole) of finely ground, anhydrous stannous chloride in 50 ml. of ether maintained at −10°, was added, dropwise, 0.135 mole (3 equivalents) of phenyllithium dissolved in 137 ml. of ether. When one equivalent (0.045 mole, 46 ml.) had been added, the reaction mixture was orange-colored; with two equivalents (0.09 mole, 91 ml.) the color was deep red; with three equivalents (0.135 mole, 137 ml.) the color was light tan. Color Test I[6] was negative upon completion of the addition of all (137 ml.) of the phenyllithium solution.

General Procedure for the Reaction of Triphenyltin-lithium with a Halide.—To a well-stirred suspension of triphenyltin-lithium in ether was added an ether solution of the appropriate halide. Unless otherwise stated the reaction mixture was then refluxed for 1.5 hours and hydrolyzed by pouring into a saturated ammonium chloride solution.

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(1) H. Gilman, L. Summers and R. W. Leeper, THIS JOURNAL, **74**, in press (1952); see also E. Bindschadler and H. Gilman, *Proc. Iowa Acad. Sci.*, **48**, 273 (1941) [*C. A.*, **36**, 1595 (1942)].

(2) H. Gilman, L. Summers and S. D. Rosenberg, THIS JOURNAL, **74**, in press (1952).

(3) G. Wittig, F. J. Meyer and G. Lange, *Ann.*, **571**, 167 (1951); see also G. Wittig, *Angew. Chem.*, **62**, 231 (1950).

(4) "Stannochlor" purchased from Metal and Thermit Corporation.

(5) See E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen," Gebruder Borntraeger, Berlin, 1937, p. 355, for a discussion of the color of solutions of diaryltin compounds in organic solvents.

(6) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

(7) In the lead series Color Test I becomes positive between 2.8 and 3.0 equivalents of phenyllithium.