The Utilization of Organolithium Compounds for the Preparation of Tertiary Phosphines, Phosphine Oxides, and Phosphine Sulfides

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Six trialkyl-, triaryl-, or alkylarylphosphines have been prepared by condensing organolithium compounds with phosphorus trichloride or phenylphosphonous chloride. A number of methods have been investigated for the conversion of these phosphines into the corresponding oxides, sulfides, and selenides. A convenient preparation of tertiary phosphine sulfides was developed. This involved the reaction of the mercuric chloride adduct of the tertiary phosphine with ammonium polysulfide. Although Grignard reagents have been reported to react with thiophosphoryl chloride to give tetrasubstituted bisphosphine disulfides, methyllithium produced only trimethylphosphine sulfide. It appears that the previously reported properties of trimethylphosphine sulfide are in error. Trialkylphosphines, in particular, have been shown to react readily with carbon tetrachloride and the carbon disulfide adducts of these phosphines have been found to react also with carbon tetrachloride.

Relatively little is known concerning the utilization of organolithium compounds, especially alkyllithium reagents, for the production of tertiary phosphines and their derivatives. Mikhailov and Kucherova[2] condensed aryllithium derivatives with phosphorus trichloride and phosphorus oxychloride to give triarylphosphines and triarylphosphine oxides. Willians[3] reported good yields of phosphines and phosphine oxides when phenyllithium was caused to react with various esters of phosphorous and phosphoric acids and dialkyl phosphorochloridates. Gilman and Stukwisch[4] found that phenylphosphonous chloride reacts smoothly with organolithium compounds, such as *p*-aminophenyllithium, to yield the expected tertiary phosphine.

A variety of methods has been utilized for the production of tertiary phosphines.[5] These include the reaction of Grignard reagents with the triesters of phosphorous acid or the corresponding acid halides, the reaction of metallic phosphides with alkyl halides, the condensation of organozinc compounds with phosphorus trihalides, the Wurtz reaction between phosphorus halides and aryl halides and the reaction between Grignard reagents and phosphorus trisulfide or phosphorus heptasulfide.

Tertiary phosphine oxides have also been prepared in a variety of ways.[6] The tertiary phosphine is often converted into the oxide by means of oxygen, nitric acid, nitrous oxide, chromic acid, potassium chlorate, peroxides, and a variety of other oxidizing agents. Another method involves the addition of a halogen to the phosphine followed by the hydrolysis of the tertiary phosphine dihalide. Grignard and organozinc reagents may react with the halides or ester of phosphorus acids to give tertiary phosphine oxides and such products may also be the result of the thermal decomposition of quaternary phosphonium hydroxides, alkoxides, or certain salts and the Arbuzov rearrangement of alkyl dialkylphosphinites.

Tertiary phosphine sulfides have been produced in similar ways;[6] however, thiophosphoryl chloride has been shown to react in a surprising fashion with Grignard reagents.[7] In this reaction a tetra-substituted bisphosphine disulfide is usually produced in high yield.

Tertiary phosphine selenides have been prepared only by the addition of elemental selenium to the corresponding phosphine.[6]

Since we have been unable to find any report of the reaction of aliphatic and alicyclic lithium derivatives with phosphorus trichloride, phosphorus oxychloride, and thiophosphoryl chloride, we decided to determine the applicability of such organolithium compounds for the synthesis of tertiary phosphines, phosphine oxides, and phosphine sulfides. In addition, we desired certain phosphine oxides, sulfides, and selenides in order to study some of their complexes with halogens. It was found that the methyl-, ethyl-, *n*-propyl-, *n*-butyl-, and cyclohexyllithium reagents condensed with phosphorus trichloride and cyclohexyllithium reacted with phenylphosphonous chloride to produce fair yields of the corresponding tertiary phosphines. Because of the exploratory nature of this work, we believe higher yields could be obtained for most of these reactions.

When phosphorus oxychloride was condensed with methyllithium or *n*-propyllithium and water was added to the reaction mixture, the organophosphorus products were taken into the water layer along with the inorganic salt. The desired phos-

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(1) To whom inquires should be directed. This paper is taken from the M. S. thesis of Constantinos Screttas, 1961.

(2) B. M. Mikhailov and N. F. Kucherova, *Dokl. Akad. Nauk SSSR*, **74**, 501 (1950); *Zh. Obshchei Khim.*, **22**, 792 (1952).

(3) J. L. Willians, *Chem. Ind.* (London), 235 (1957).

(4) H. Gilman and C. G. Stukwisch, *J. Am. Chem. Soc.*, **63**, 2844 (1941).

(5) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, 1950, p. 10.

(6) Ref. 5, p. 98.

(7)(a) M. I. Kabachnik and E. S. Shepeleva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, No. 1, 56 (1949). (b) G. M. Kosolapoff and R. M. Watson, *J. Am. Chem. Soc.*, **73**, 5466 (1951). (c) H. Reinhardt, D. Bianchi, and D. Molle, *Ber.*, **90**, 1656 (1957). (d) H. Niebergall, *Angew. Chem.*, **72**, 210 (1960).

phine oxides could not be isolated readily from such a mixture. In one instance an attempt was made to isolate trimethylphosphine oxide from a water solution containing lithium chloride by passing the solution alternately through cation and anion exchange resins. This was only partially successful when a portion of the phosphine oxide appeared to have been absorbed by the cation exchange resin and an additional quantity of the phosphine oxide appeared to have been lost because of its volatility during the evaporation of the water solutions. A small amount of what appeared to be somewhat impure trimethylphosphine oxide was isolated from this reaction.

We were also unable to isolate any tricyclohexylphosphine oxide from the reaction between cyclohexyllithium and phosphorus oxychloride. Issleib and Brack[8] also failed to prepare tricyclohexylphosphine oxide from cyclohexylmagnesium halide and phosphorus oxychloride. The reason for these failures is not understood. Molecular models show that from a steric point of view tricyclohexylphosphine, recovered in 28% yield from the reaction between cyclohexyllithium and phosphorus trichloride, should be essentially as difficult to produce as tricyclohexylphosphine oxide. However, Issleib and Tzschach[9] were able to prepare tricyclohexylphosphine sulfide from cyclohexylmagnesium chloride and thiophosphoryl chloride, even though the sulfur atom of the thiophosphoryl chloride molecule is more bulky than the oxygen atom of phosphorus oxychloride. Since we attempted to carry out the reaction between cyclohexyllithium and phosphorus oxychloride in pentane, there is the possibility that the reaction might be successful if attempted in a more polar solvent.

In 1857 Cahours and Hofmann[10] reported the synthesis of trimethylphosphine sulfide by the addition of sulfur to the corresponding phosphine. They reported their sulfide melted at 105°, but they gave no analysis for the substance.

More recently Malatesta[11] isolated a compound melting at 105° from the reaction between phosphorus pentasulfide and methylmagnesium halide. He apparently identified this compound as trimethylphosphine sulfide because its melting point duplicated the value reported by Cahours and Hofmann. Methylmagnesium halide and thiophosphoryl chloride have been reported to give tetramethylbisphosphine disulfide, melting at 205–213° (Kabachnik and Shepeleva[7a]) and at 226.5–227.5° (Reinhardt, *et al.*),[7c] insoluble in water, ethanol, and ether.

From the reaction between methyllithium and thiophosphoryl chloride we isolated a compound which does not resemble either of the above mentioned substances. It melted at 154°, was soluble in water, ethanol, and ether, and its elemental analysis and molecular weight clearly indicated that this compound was trimethylphosphine sulfide. It appears that Cahours and Hofmann and Malatesta either isolated a very impure form of trimethylphosphine sulfide or they obtained some entirely different material.

Whereas the addition of sulfur to the tertiary phosphines in the absence of a solvent gave low yields of the phosphine sulfides, the reaction between the mercuric chloride adduct of the tertiary phosphines and ammonium polysulfide in ethanol solution gave the desired phosphine sulfides in good yields and excellent purity. This is a new and desirable synthesis of phosphine sulfides.

In the course of this work we found that certain tertiary phosphines reacted vigorously when added to carbon tetrachloride. This appeared surprising in view of the fact that carbon tetrachloride has been suggested as an "inert" solvent for the reaction between phosphines and halogens,[12] for the quaternization of phosphines,[13] and for the reaction between elemental sulfur and secondary phosphines.[14] We found two papers published by Hofmann[15] approximately a century ago which discussed the reaction between phosphines and carbon tetrachloride. For example, with triethylphosphine a complex phosphonium salt is supposed to result as follows:

$$\mathrm{CCl_4 + 3(C_2H_5)_3P \longrightarrow ClC\{[(C_2H_5)_3P]Cl\}_3}$$

Table I shows semiquantitatively the behavior of phosphines when mixed with carbon tetrachloride. Tertiary phosphines containing two or more alkyl groups were found to react rapidly with carbon tetrachloride at room temperature.

TABLE I

REACTIVITY OF PHOSPHINES WITH CARBON TETRACHLORIDE

Phosphine	Observed reaction
Tri-*n*-propyl-	Burns
Tri-*n*-butyl-	Very vigorous, even at low temperature
Dicyclohexylphenyl-	Vigorous
Triphenyl-	No reaction, even at elevated temperatures and in the presence of $AlCl_3$

The solid tertiary alkylphosphine–carbon disulfide adducts react also with carbon tetrachloride but at a much slower rate than the phosphines. The trimethylphosphine–carbon disulfide adduct reacted with carbon tetrachloride to give a water-soluble product containing the chloride ion. From this was isolated a solid possessing the properties of

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[8] K. Issleib and A. Brack, *Z. anorg. allegem. Chem.*, **277**, 258 (1954).

[9] K. Issleib and A. Tzschach, *Ber.*, **92**, 704 (1959).

[10] A. Cahours and A. J. Hofmann, *Ann.*, **104**, 1 (1857).

[11] L. Malatesta, *Gazz. chim. ital.*, **77**, 509 (1947).

[12] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, 1950, p. 58.

[13] R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 3631 (1956).

[14] G. Peters, *J. Am. Chem. Soc.*, **82**, 4751 (1960).

[15] A. W. Hofmann, *Proc. Roy. Soc.* (London), **10**, 189 (1859); **11**, 290 (1861). These papers appear to have been overlooked by Beilstein's "Handbuch der organischen Chemie" and similar reference sources.

trimethylphosphine sulfide. The triethylphosphine–carbon disulfide adduct behaved similarly, yielding what appeared to be triethylphosphine sulfide.

Tertiary phosphine selenides were produced by fusing the phosphine with elemental selenium in the absence of a solvent. The resulting selenides were difficult to purify and were somewhat unstable.

Experimental[16]

Reagents.—Ether was anhydrous, reagent grade, and was used after drying over sodium metal. Lithium metal was purchased from Lithium Corporation of America, Inc. Phosphorus trichloride, reagent grade, was purchased from Mallinckrodt Chemical Works and used without purification. Phenylphosphonous chloride was kindly donated by Victor Chemical Works and was used without purification. Alkyl halides and thiophosphoryl chloride were purchased from the Matheson Coleman and Bell Company and used without further purification. Some of the thiophosphoryl chloride was kindly supplied by Victor Chemical Works. Pentane, technical grade, 95 mole % minimum, was purchased from Phillips Petroleum Co. and used after drying over sodium. Selenium metal powder was used as purchased from E. H. Sargent and Co. Ammonium polysulfide (Baker's analyzed reagent) contained 25% $(NH_4)_2S$ and 5–6% dissolved sulfur.

General Experimental Procedure.—In all experiments a three-necked round bottom flask was used. In the center neck was fitted a glass stirrer which passed through a glass bearing, lubricated with castor oil and sealed from the atmosphere by a rubber sleeve. In one of the side necks was fitted a Friedrichs condenser and to the other side neck was attached a pressure-equalizing dropping funnel. A slow stream of nitrogen or helium was passed through the apparatus to maintain an inert atmosphere during the reaction.

The various organolithium reagents were prepared according to directions reported in the literature. However, at times slight modifications were necessary. Satisfactory yields of ethyllithium and *n*-propyllithium resulted from reactions carried out at −30° to −10°. The double titration method[17] was used for the determination of the yields of the lithium compounds prepared when ether was the solvent.

The molecular weights were determined with a Washburn and Read apparatus.[18]

General Preparation of Phosphines. Method A.—To the organolithium reagent in ether was added a solution of phosphorus trichloride in ether at the reaction temperature indicated in Table II. The mixture was heated to reflux for 1–2 hr., an excess of 10% sodium hydroxide solution was added cautiously with cooling and the mixture was cooled in a Dry Ice–acetone bath until the water layer was frozen. The upper layer was decanted into an Erlenmeyer flask containing approximately 300% excess carbon disulfide. Generally the carbon disulfide adduct separated as a crystalline solid, was collected on a filter, washed with a small amount of petroleum ether, and dried for a brief time. With the higher molecular weight tertiary alkylphosphines it was necessary to cool the solution in a Dry Ice–acetone bath in order to cause the majority of the adduct to crystallize.

Method B.—Method A, except the carbon disulfied adduct was not prepared. Instead, the phosphine itself was recovered by fractional distillation or crystallization.

Method C.—Method A, except that the reaction solvent was pentane instead of ether and, after hydrolysis with excess sodium hydroxide solution, the two immiscible layers were separated in a separatory funnel under an atmosphere of nitrogen.

Method D.—Method B, except the reaction solvent was pentane instead of ether and after hydrolysis with excess sodium hydroxide solution the two immiscible layers were separated in a separatory funnel under an atmosphere of nitrogen.

The preparation of phosphines is summarized in Table II.

Phosphine Oxides.—The phosphine oxides were prepared as indicated in Table III.

Special mention should be made of the attempt to prepare and isolate trimethylphosphine oxide. To a solution of methyllithium[19] prepared from 1 g.-atom of lithium, 25.5 g. (0.167 mole) of phosphorus oxychloride, diluted with 100 ml. of ether, was added dropwise. The resulting mixture was filtered and the filtrate was evaporated to dryness leaving only a trace of oily residue. Since virtually all the product was in the ether-insoluble fraction, this pale yellow solid was dissolved in 500 ml. of water, and the solution was filtered and passed alternatively through a column of Dowex 50 resin (H^+ form) and Dowex 2 resin (OH^- form) until the eluate was neutral. The relatively large volume of combined eluate and column washings was evaporated to dryness in a rotating vacuum evaporator. There remained only 2.5 g. of viscous oil which slowly solidified in a desiccator but which absorbed water so rapidly when removed from the desiccator that no satisfactory melting point could be determined. A portion of this crude solid was sublimed at 100–130° at 1 mm. This sublimed solid, when it was not exposed to moisture, melted at 130°. It has been reported to melt at 140–141°.[20] Apparently the Dowex 50 resin absorbed some of this same product because when the resin was washed with a small quantity of 2 *N* hydrochloric acid and the washings were evaporated to dryness, there remained an additional 2 g. of viscous residue which possessed the same properties as the neutral product above. Thus, 4.5 g. of crude trimethylphosphine oxide (29%) was recovered and a considerable quantity is believed to have been lost while evaporating the aqueous solutions to dryness under vacuum because of the pronounced volatility of this material.

Reaction of Methyllithium with Thiophosphoryl Chloride.—At −30° 19 g. (0.17 mole) of thiophosphoryl chloride and 150 ml. of ether were added to 0.65 mole of methyllithium in 600 ml. of ether. After standing overnight at room temperature the mixture was heated to reflux for 1 hr., the solvent was removed by distillation and the solid residue was extracted for 24 hr. in a Soxhlet apparatus with ether. The extracted solid was recrystallized twice from a mixture of isopropyl alcohol and petroleum ether and once from absolute alcohol. The white needles weighed 9 g. and melted at 154°.

Anal. Calcd. for C_3H_9PS (trimethylphosphine sulfide): C, 33.31; H, 8.38; P, 28.66. Mol. wt. 108.15. Calcd. for $C_4H_{12}P_2S_2$ (tetramethylbisphosphine disulfide): C, 25.79; H, 6.49; P, 33.26. Mol. wt. 186.23. Found: C, 33.01, 33.27; H, 8.61, 8.32; P, 28.58, 28.62. Mol. wt., (ebullioscopic) 108.9.

The analytical data clearly indicates that this product was trimethylphosphine sulfide in a yield of 49%, basis thiophosphoryl chloride.

Tricyclohexylphosphine Sulfide.—Five grams of tricyclohexylphosphine and 0.55 g. of sulfur were heated under a nitrogen atmosphere at 150° until the mixture solidified. The crude product was dissolved in alcohol, decolorized with carbon, and recrystallized several times from alcohol to a

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[16] All melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories of Knoxville, Tenn.

[17] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

[18] E. W. Washburn and J. W. Read, *ibid.*, **41**, 729 (1919).

[19] Prepared by method of C. Tegner, *Acta Chem. Scand.*, **6**, 782 (1952), substituting methyl chloride for methyl iodide.

[20] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

TABLE II

PHOSPHINES

Phosphine	Method of prep.	Reagents	Reaction temp., °C.	Yield of CS_2 ad-duct, %	Yield of phos-phine, %	M.p. of CS_2 adduct, °C.	M.p. or b.p. of phosphine, °C.
Trimethyl-	A	$CH_3Li^a + PCl_3$ (0.52 mole)(0.15 mole)	−20 to −10	66	..	119 (from 95% ethanol)	...
Triethyl-	A	$C_2H_5Li + PCl_3$ (0.26)(0.05 mole)	−40	62	..	118–120[b] (from methanol)	...
Tri-*n*-propyl-	B	$n\text{-}C_3H_7Li^c + PCl_3$ (0.5 mole)(0.14 mole)	−20 to −30	..	45	...	88–93 (31 mm.)[d] (b.p.)
Tri-*n*-butyl-	A	$n\text{-}C_4H_9Li + PCl_3$ (0.34 mole)(0.09 mole)	−10	55	..	65[e]	...
Triphenyl-	B	$C_6H_5Li + PCl_3$ (0.85 mole)(0.25 mole)	15	..	62	...	79[f] (from acetic acid) (m.p.)
Tricyclohexyl-	C	$C_6H_{11}Li^g + PCl_3$ (0.175 mole)(0.05 mole)	−30	28	..	116–118[h] (from pet. ether)	...
Dicyclohexylphenyl-	D	$C_6H_{11}Li + C_6H_5PCl_2$ (0.33 mole)(0.1 mole)	0 to 5	..	90	...	56–57 (from acetone) (m.p.)

[a] Prepared by the method of C. Tegner, *Acta Chem. Scand.*, **6**, 782 (1952), substituting methyl chloride for methyl iodide. [b] Reported m.p. 121–122°, J. P. Wibaut, *Rec. trav. chim.*, **44**, 239 (1925). [c] Prepared by method for *n*-butyllithium, H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949). [d] Reported b.p. 77° (13 mm.), E. Rothstein, R. W. Saville, and P. E. Horn, *J. Chem. Soc.*, 3994 (1953). [e] Reported m.p. 65.5°, W. C. Davies and W. J. Jones, *ibid.*, 33 (1929). [f] Reported m.p. 80°, P. Walden and R. Swinne, *Z. physik. Chem.*, **79**, 700 (1912). [g] Prepared by method of T. D. Perrine and H. Rapoport, *Anal. Chem.*, **20**, 635 (1948). [h] Reported m.p. 118°, see ref. 8.

TABLE III

PHOSPHINE OXIDES

Phosphine oxide	Method of prep.	Yield	M.p., °C.
Triphenyl-	Michaelis and Gleichmann[a] from 20 g. $(C_6H_5)_3P$, 15 g. Br_2 and 10% NaOH	16 g., 75%	156 from alcohol–H_2O[b]
Tricyclohexyl-	Issleib and Brack,[c] from 12 g. $(C_6H_{11})_3P$ and excess $KMnO_4$ in acetone	8 g., 65%	155 from acetone[d]
Dicyclohexylphenyl-	Same as for tricyclohexylphosphine oxide,[c] from 14 g. $(C_6H_{11})_2C_6H_5P$	11.5 g., 77%	157.5 from acetone[e]
Cyclohexyldiphenyl-	From 0.22 mole C_6H_5Li, and 18.1 g. $C_6H_{11}POCl_2$ in Et_2O at 0–5°. Hydrolyzed with 200 ml. 10% NaOH, Et_2O layer separated, evaporated	15.9 g., 58%	165 from alcohol–H_2O[g]

[a] A. Michaelis and L. Gleichmann, *Ber.*, **15**, 801 (1882). [b] Lit. 156°, see ref. 2. [c] Ref. 8. [d] Lit. 155–157°, see ref. 8. [e] *Anal.* Calcd. for $C_{18}H_{27}PO$: C, 75.05; H, 9.12; P, 10.70. Found: C, 74.69, 74.82; H, 9.13, 9.16; P, 10.76, 10.86. [f] A. F. Isbell and F. T. Wadsworth, *J. Am. Chem. Soc.*, **78**, 6042 (1956). [g] L. Horner, H. Hofmann, and H. G. Wippel, *Ber.*, **91**, 64 (1958), gave m.p. 165–166°.

melting point of 185° (lit. m.p. 182°).[8] The yield was 1.5 g. (30%).

Dicyclohexylphenylphosphine Sulfide.—The phosphine–mercuric chloride adduct was prepared by adding the phosphine to a slight excess of a saturated alcoholic solution of mercuric chloride. Twelve grams of this adduct was suspended in a solution containing 50 ml. of ammonium polysulfide and 100 ml. of 95% ethanol. While heating the mixture under reflux for 45 min., red mercuric sulfide precipitated. This precipitate was filtered from the hot mixture and washed with 100 ml. of alcohol. Cooling the filtrate to room temperature caused the phosphine sulfide to separate in large crystals which weighed 4 g. (66%) and melted at 168°.

Anal. Calcd. for $C_{18}H_{27}PS$: C, 70.77; H, 8.58; P, 10.14. Found: C, 70.54, 70.79; H, 8.78, 8.63; P, 9.90, 9.98.

Triphenylphosphine Sulfide.—The preparation of this compound was the same as that for dicyclohexylphenylphosphine sulfide. From 5 g. of triphenylphosphine, 30 ml. of ammonium polysulfide solution, and 100 ml. of alcohol 4.5 g. (80%) of triphenylphosphine sulfide was obtained, m.p. 161°, after one recrystallization from alcohol (lit. m.p. 161°).[21]

Phosphine Selenides.—The phosphine selenides were prepared by heating the phosphine with elemental selenium at a temperature of 150–200° for 1 hr. The crude product was extracted either with hot carbon disulfide or hot benzene to separate it from unreacted selenium. After crystallizing the product from benzene or evaporating the extract to dryness, the phosphine selenide was recrystallized several times from alcohol.

Table IV summarizes the preparations of the phosphine selenides.

TABLE IV

PHOSPHINE SELENIDES

Phosphine selenide	Reagents Phosphine, g.	Selenium, g.	Reaction temp., °C.	Yield, %	M.p., °C.
Triphenyl-	20	8	180–200	46	187–188[a]
Tricyclohexyl-	10	3	150–160	30	192[b]
Dicyclohexylphenyl-	5	1.5	180	63	166[c]

[a] A. Michaelis and H. Soden, *Ann.*, **229**, 295 (1895) gave m.p. 184–186°. [b] *Anal.* Calcd. for $C_{18}H_{33}PSe$: C, 60.15; H, 9.25; P, 8.48. Found: C, 60.38, 60.58; H, 9.33, 9.51; P, 8.38, 8.43. [c] *Anal.* Calcd. for $C_{18}H_{27}PSe$: C, 61.36; H, 7.43; P, 8.79. Found: C, 61.17, 61.18; H, 7.71, 7.84; P, 8.66, 8.76.

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[21] W. Strecker and C. Grossmann, *Ber.*, **49**, 63 (1916).

Action of Carbon Tetrachloride on the Carbon Disulfied Adducts of Trimethyl- and Triethylphosphine.—Three grams each of the two carbon disulfide adducts were suspended in 50 ml. of carbon tetrachloride in a stoppered flask. During several hours standing the characteristic red color of the adduct disappeared and an oily product collected on the surface of the solvent. Evaporation of the solvent left an oil from which crystals formed slowly. The following quantitative observations were made: (1) The semisolid residue was completely soluble in water, (2) it was acidic to litmus, (3) silver nitrate gave a white precipitate, (4) no sulfide ions were detected with lead acetate, and (5) the characteristic odor of the phosphine (which exists in the carbon disulfide adduct) was no longer detectable.

The residue from the trimethylphosphine adduct was recrystallized from alcohol and produced a white solid melting at 154°. When an authentic sample of trimethylphosphine sulfide, prepared from methyllithium and thiophosphoryl chloride, was mixed with this solid, the melting point was not depressed.

When the residue from the triethylphosphine adduct was recrystallized from alcohol, a white solid melting at 94° was recovered. Although triethylphosphine sulfide has been reported[10] to melt at 94°, no authentic sample of this compound was available for comparison. Therefore, this compound was analyzed.

Anal. Calcd. for $C_6H_{15}PS$: C, 47.98; H, 10.06; P, 20.62. Found: C, 47.97, 48.09; H, 9.95, 10.20; P, 20.62, 20.62.

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Synthesis of Polyfluorinated Heterocycles by Indirect Fluorination with Silver Fluorides. I. Fluoro-s-triazines and Reactions of Cyanuric Fluoride[1]

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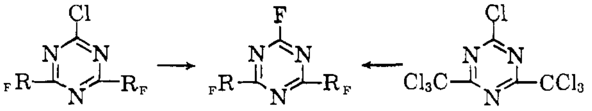
The conversion of chloro-*s*-triazines to the corresponding fluoro-*s*-triazines by means of several inorganic fluorinating agents was studied. Silver fluoride was found to be most useful for this purpose. Reactions of cyanuric fluoride with alcohols, amines, and diazomethane are described.

As part of a comprehensive study of the preparation of fluorinated heterocyclic compounds, possibilities for the conversion of chloro-*s*-triazines to the corresponding fluoro-*s*-triazines by means of inorganic fluorinating agents were investigated. At the time this study was undertaken, the conversion of cyanuric chloride into cyanuric fluoride by means of potassium fluorosulfinate[3] or sulfur tetrafluoride[4] had not been reported; however, this transformation had been achieved by means of antimony trifluoride dichloride (Swarts reagent).[5,6] The latter reagent converted 2,4-bis(trichloromethyl)-6-chloro-*s*-triazine (VI) easily into 2,4-bis(trifluoromethyl)-6-fluoro-*s*-triazine (III),[5] but when applied to the conversion of 2,4-bis(perfluoroalkyl)-6-chloro-*s*-triazines (I and II) into the perfluorinated triazines (IV and V), the reaction gave low yields.



I. $R_F = CF_2CF_3$
II. $R_F = CF_2CF_2CF_3$
III. $R_F = CF_3$
IV. $R_F = CF_2CF_3$
V. $R_F = CF_2CF_2CF_3$
VI

Therefore, other fluorinating agents were investigated for the preparation of the higher homologs of III from the readily accessible 2,4-bis(perfluoroalkyl)-6-chloro-*s*-triazines.[7] 2,4-Bis(pentafluoroethyl)-6-chloro-*s*-triazine (I) was selected as the prototype for this study.

With mercuric fluoride, only partial conversion of the chlorotriazine (I) to the desired perfluorinated triazine (IV) could be achieved, even when the reactants were heated for several hours. In contrast to this result, silver difluoride reacted vigorously with I to give IV in good yield, but it was difficult to control the very exothermic reaction. The reaction of I with silver fluoride required heating, proceeded smoothly, and gave an almost quantitative yield.

Lead difluoride, a very mild fluorinating agent, did not react at all with compound I even at reflux temperature, but was found to be very useful for the purification of 2,4-bis(perfluoro-

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[2] (a) To whom inquiries should be directed. (b) Olin Mathieson Chemical Corporation, New Haven, Conn.

[3] D. W. Grisley, Jr., E. W. Gluesenkamp, and S. A. Heininger, *J. Org. Chem.*, **23**, 1802 (1958).

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