Part II

PHYSICAL PROPERTIES EVALUATION OF COMPOUNDS AND MATERIALS

Some Phosphines, Phosphine Sulfides, and Phosphine Selenides

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The preparation and properties of 16 new phosphine sulfides and phosphine selenides are reported. The sulfides and selenides are prepared by fusion of the phosphines with the elements in a dry, nitrogen atmosphere. Preparation of the phosphines is accomplished by condensation of a phosphorous trihalide, or substituted halide with the Grignard reagent or the lithium alkyl in an inert atmosphere. The sulfides and selenides are colorless solids, or yellow, high boiling, viscous liquids.

AS PART OF an over-all study concerned with the location and nature of the fundamental $P \rightarrow X$ stretching frequency, where X is a group *VI* atom, a representative number of phosphine sulfides and selenides were needed. With the exception of triphenylphosphine sulfide, such compounds are not commercially available and only a relatively small number have been prepared and characterized. A total of 35 tertiary phosphine sulfides have been listed by Kosolapoff (*7*) of which four are trialkyl derivatives. The vast majority of those listed are phenyl-substituted derivatives. The same source lists seven phosphine selenides, two of which are trialkyl derivatives. Tricyclohexylphosphine sulfide has been reported (*5*, *15*); and dicyclohexylphenylphosphine sulfide and selenide, tricyclohexylphosphine selenide (*15*), tri-*n*-butylphosphine sulfide (*17*), tris-(2-carbethoxyethyl)phosphine sulfide (*13*), diphenylvinylphosphine sulfide, and several secondary phosphine sulfides (*11*) have been prepared recently. Michaelis (*10*) reported phenyldiethylphosphine sulfide, but no physical properties were given.

We have extended considerably the number of these compounds. These are described along with a few others previously prepared in order to add to our knowledge of their properties, and, in some cases, such as trimethylphosphine, to provide a more accessible and efficient method of synthesis.

PREPARATIONS

Trimethylphosphine. Although the preparation of this compound has been described previously, the following method yields the pure compound directly from the reaction mixture and avoids contamination with diethyl ether which has an almost identical boiling point. This compound burns violently in air and the vapors are highly toxic. The use of a dry, oxygen free atmosphere is absolutely essential.

A 2-liter, three-necked, oven dried flask was fitted with a stirrer and a 250 ml. dropping funnel. It is recommended that the dropping funnel be attached to one opening of a parallel side arm joint, the other opening being used as the nitrogen inlet. A drying tower was included between the nitrogen tank and the reaction vessel. To the third neck of the flask was attached a small Vigreaux column which leads, by way of a one-way stopcock, directly to an all glass, unjointed system of at least three consecutive U-tubes, each of about 50 ml. capacity having constricted inlets and outlets. The final U-tube outlet is attached to a $CaCl_2$-P_2O_5 drying tower and then to a sulfuric acid bubbling tower so as to be able to observe a positive nitrogen pressure. The first U-tube is immersed in a Dewar flask containing a cooling bath which is maintained at least −70° C.

After the dry equipment is assembled and nitrogen flushed, a solution containing about 2.4 moles of methylmagnesium bromide in 800 ml. of alcohol free, sodium dried and distilled di-*n*-butyl ether is prepared in the usual manner from *n*-butyl bromide and magnesium. At 0° C. the dropwise addition of a solution of 68 ml. of phosphorous trichloride in 100 ml. of *n*-butyl ether, over a period of two hours is carried out with stirring. The stirring is continued at room temperature for an hour after which the stirrer and the dropping funnel inlet are replaced with stoppers so that the only outlet remaining is that which leads to the U-tube system. The temperature of the reaction flask is very gradually raised by means of a heating mantle to 120–150° C. to decompose the magnesium halide adduct. About 20 ml. of liquid is collected in the first U-tube. The flask is then cooled to room temperature and the stopcock leading to the first U-tube is closed while the first U-tube is warmed to 42° C., transferring the phosphine to the second U-tube where it is condensed in the dry-ice-acetone bath. The inlet constriction to the second tube is then flame sealed with extreme care. The fractionation is then repeated from U-tube-2 to U-tube-3. Both ends of the sample tube are then flame sealed. Our samples were collected over a temperature range of 37–39° C. when distilled. The boiling point of trimethylphosphine has been reported as 37.8° C. (*14*).

Triethylphosphine. Triethylphosphine was readily prepared by the action of phosphorous trichloride on ethylmagnesium bromide. We found the isolation and separation of this compound to be much more easily accomplished, and the yields increased, if the hydrolysis was eliminated and the phosphine distilled directly from the reaction mixture in a dry nitrogen atmosphere following distillation of the ether.

Other Phosphines. All of the other phosphines described were prepared either by the reaction of a phosphorous trihalide or the mono- or disubstituted phosphorous halide with the appropriate Grignard reagent in ether (method I); or by condensation with the lithium alkyl in heptane (method II). The organic solvents containing the phosphine were then hydrolyzed in the usual manner (*6*) the ether layer dried over sodium sulfate and the phosphine was then vacuum distilled after removal of the ether.

Phosphine Sulfides and Selenides. All of these derivatives could be prepared by direct combination of the element with the phosphine. Since most of these compounds were high boiling liquids it was convenient to carry out the reaction in a flask which then served as a distillation vessel.

All flasks were oven dried and thoroughly nitrogen flushed, and the nitrogen atmosphere was maintained throughout the course of the reaction in order to eliminate formation of the oxide. Transfer of the phosphines was most easily accomplished by means of a glass syringe.

A slight excess of sulfur, or selenium powder was added to the phosphine, the reactions usually being highly exothermic. After addition of all of the solid, the mixture was fused over an open flame for five minutes, the temperature not exceeding the boiling point of the phosphine. Purification was carried out by recrystallization, usually from ethanol, or vacuum distillation. In many cases it was necessary to evaporate the sample almost to dryness in order to recover the crystalline derivative.

Contamination by sulfur presented a problem, expecially in the case of the solids. Generally, the sulfur was less soluble than the phosphine sulfide and purification could be accomplished by several recrystallizations, usually from ethanol.

In some instances the phosphine was not separated as a pure compound. In these cases the sulfur or selenium was allowed to react with the crude phosphine and the derivative subsequently purified. The list of compounds prepared along with pertinent physical data, is given in Table I.

DISCUSSION

When it was possible to do so, the separation of the phosphine was accomplished without hydrolysis of the reaction mixture. In those cases where both methods could be compared, the yield of the phosphine was significantly increased by elimination of hydrolysis. However, only when the solid phase separated as a dense, easily filtered precipitate, could hydrolysis be eliminated as a separate stop. In most cases, the Grignard reagent-phosphorous halide reaction mixture was obtained as an almost continuous, semi-solid mass separable only after aqueous acid hydrolysis. The yields of phosphines were almost always in the 50–75% range if sufficient care was taken to eliminate oxygen and moisture. Yields as high as 85% were obtained in the preparation of phosphines hearing phenyl substituents.

The yields of phosphine sulfides, or selenides, following purification, were 40–60% based upon the amount of phosphine used. Yields of up to 90% of pure material were possible when the product was an easily crystallizable solid.

The characterization of trialkylphosphine chalcogenides is now complete through the *n*-C_5 series. The trimethyl compound, in every case is a highly crystalline solid. There is an abrupt drop in the melting point of the oxides, beginning with the triethyl derivative, m.p. 50° C., which then varies very little with increasing length of the alkyl chain. The entire series, from the triethyl through the tri-*n*-octylphosphine oxide are colorless, waxy solids melting in a 50–60° C. range.

Table I. Phosphines, Phosphine Sulfides and Phosphine Selenides

			Analytical Data		Physical Properties					
Compound	Method		Calcd.	Found	Color	M.P. (° C.)	B.P. (° C.)	Refractive index^{a}	Previously reported^{b}, B.P. (° C.)	Yield, %^{c}
(*n*-Propyl)$_3$phosphine	I				colorless		180°(740)^{d}		187.5°(760)^{3} 103.5°(50)^{3}	80
(*n*-Propyl)$_3$phosphine sulfide		C	56.21	56.11	pale yellow		112°(1.1)	1.5071(27)		61
		H	11.01	11.23						
		S	16.67	16.62						
(*n*-Propyl)$_3$phosphine selenide		C	45.19	45.40	colorless crystals	32	116°(0.95)			45
		H	8.84	8.67						
		P	12.95	13.00						
(*n*-Butyl)$_3$phosphine	II				colorless		63°(0.80)	1.4634(25)	129°(22)^{9} 136°(32.5)^{9} 140.5°(50)^{14}	69
(*n*-Butyl)$_3$phosphine selenide		C	51.24	50.86	pale yellow		150–151°(0.80)	1.5150(27)		51
		H	9.67	9.36						
		P	11.02	11.12						
(*n*-Amyl)$_3$phosphine	I				colorless solid	31	107°(0.75)		185.5(50)^{3} 165°(19)^{3} m.p. 29° C.^{9}	63
(*n*-Amyl)$_3$phosphine sulfide		C	65.16	64.87	yellow-orange		165–167°(0.90)	1.4902(29)		48
		H	12.03	12.15						
		S	11.64	11.64						
(*n*-Amyl)$_3$phosphine selenide		C	55.71	56.00	pale yellow, extremely viscous		158°(0.75)^{e}	1.5055(25)		61
		H	10.29	10.48						
		P	9.58	9.71						
Phenyldimethylphosphine sulfide		C	56.44	56.24	colorless	42				78
		H	6.52	6.35						
		S	18.84	19.03						
Phenyldimethylphosphine selenide		C	44.25	44.40	yellow, highly viscous		129°(0.90)	1.6272(27)		62
		H	5.11	4.83						
		P	14.26	14.41						
Phenyldiethylphosphine							223°(740)		221.9(atm.)^{10} 108(20)^{8}	83
Phenyldiethylphosphine sulfide		C	60.57	60.34	pale yellow, viscous		127.5°(0.80)	1.5891(25)	360(atm.)^{10}	73
		H	7.63	7.81						
		S	16.18	16.20						
Phenyldiethylphosphine selenide		C	49.11	49.39	pale yellow, viscous		149°(1.7)	1.6086(27)		52
		H	6.17	6.40						
		P	12.64	12.61						
Phenyldibutylphosphine	II				colorless				180–186(atm.)^{16}	69
Phenyldibutylphosphine sulfide		C	66.10	66.39	colorless	47				63
		H	9.04	9.18						
		S	12.85	12.90						
Phenyldibutylphosphine selenide		C	55.81	55.73	colorless	54				70
		H	7.64	7.70						
		P	10.28	10.35						
Methyldiphenylphosphine					colorless		190°(1.2)	1.6230(25)	284.(760)^{4}	84
Methyldiphenylphosphine sulfide		C	67.22	67.28	yellow, viscous		181°(1.5)	1.6515(26)		39
		H	5.64	5.60						
		S	13.81	14.06						

Methyldiphenylphosphine selenide		C H P	55.93 4.69 11.10	55.89 4.89 10.85	colorless		200°(1.35)	1.6780(26)		42
Ethyldiphenylphosphine	II				colorless		112°(1.4)		293(760)[4] 182(22)[4] 65.5–66[1]	68
Ethyldiphenylphosphine sulfide		C H S	68.67 6.14 13.02	68.64 6.07 13.18	colorless	67				88
Ethyldiphenylphosphine selenide		C H P	57.35 5.16 10.57	57.43 5.16 10.60	colorless	49				67
n-Butyldiphenylphosphine sulfide		C H S	70.04 6.98 11.65	69.76 6.94 11.97	colorless	45				83
n-Butyldiphenylphosphine selenide		C H P	59.80 5.96 9.64	59.51 5.82 9.82	colorless	63				79

[a] Values in parentheses are in °C. [b] Superscript is reference number. [c] Average of at least three trials. [d] The figure in parentheses refers to the pressure in mm. of Hg. [e] Because of the remarkably high viscosity of this compound a great deal of external heating was applied at the condenser take-off in order to get the liquid over. Since the thermometer may have been externally heated, the boiling point cannot be reported with confidence.

The trend is essentially the same in the sulfide and selenide series, with the difference that the triethyl derivative is still quite crystalline in both cases. The transition over to high boiling, viscous liquids begins with the tripropyl member of each series. To determine through what chain length this physical state persists, we much await the synthesis of additional members of these series.

The typical yellow to yellow-orange color which characterises the liquid sulfides and selenides may be due to impurities, but is probably an inherent physical characteristic of these compounds in the liquid state. On freezing, all of these compounds were observed to form completely colorless solids. Upon melting, the color is restored.

There appears to be no obvious relationship as regards the melting point of any O-S-Se series. Whereas the sulfide is the highest melting of the triethyl series, the oxide is the highest melting of the tripropyl series and the selenide is the highest melting of the tricyclohexyl series. The length of the alkyl groups undoubtedly becomes the determining factor in fixing the narrow range of melting points encountered among the higher members of each series. There is little doubt that the P-O bond is the most highly polar of the series and this may account for the fact that the oxides exist as solids at room temperature whereas the sulfides and selenides revert to liquids with increasing length of the alkyl group.

Of considerable interest is the high stability of both tricyclohexyl- and triphenylphosphine. The trialkylphosphines oxidize vigorously in air, but tricyclohexylphosphine is a stable solid. Although the stability of the triphenyl compound may be largely attributed to the electron withdrawing tendency of the phenyl groups which decrease the donor ability of the phosphorous atom, the stability of the tricyclohexyl compound must be accounted for on a structural basis. The relative stability of this molecule is probably due almost entirely to steric factors.

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