PHOSPHINE TELLURIDES

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INTRODUCTION

The first example of a phosphine telluride, tri-*n*-butylphosphine telluride, has been recently reported[1]. In the present paper the reaction of tellurium with thirteen phosphines, including trialkyl- and triphenyl-, as well as mono- and diphenyl-substituted phosphines is described. Five new phosphine tellurides were isolated and characterized. Although pure crystalline compounds were not isolated in several instances, studies of the solubility of tellurium in these phosphines indicated that the reaction may have, in fact, proceeded to a considerable extent. The extent to which the reaction proceeded clearly diminished as the number of phenyl groups on the phosphorus atom increased.

EXPERIMENTAL

Phosphines and tellurium

The phosphines used in this study were prepared in the conventional manner[2] by the reaction of the appropriate alkyl Grignard reagent with phosphorus trichloride, phenylphosphonous dichloride, or diphenylphosphinous chloride. The phosphines were redistilled at reduced pressure just prior to use.

Tellurium powder was supplied by the Canadian Copper Refiners, Ltd. and assayed as follows: 99.4 % tellurium, 0.32 % selenium and 0.06 % lead.

Preparation of phosphine tellurides

The phosphine tellurides were prepared by the direct combination of the phosphine with finely powdered tellurium in boiling toluene in an atmosphere of nitrogen. Since the preparations were very similar, only the synthesis of the tri-*n*-propyl derivative will be described in detail.

To 120 g (0.75 moles) of freshly distilled tri-*n*-propylphosphine in 350 ml of sodium-dried and distilled toluene contained in a one-necked 500 ml round-bottomed flask equipped with a reflux condenser, was added 35 g (0.27 moles)* of finely powdered tellurium. The mixture was refluxed under a nitrogen atmosphere. The tellurium powder was consumed after three hours and an additional five grams was added. After 21 hours of reflux the hot solution was filtered rapidly through a sintered glass filter, under nitrogen, in order to remove any unreacted tellurium. The yellow-orange

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* The amount of tellurium used varied, depending upon the extent to which a particular phosphine derivative reacted. If the tellurium powder was dissolved, more was added.

filtrate was evaporated under reduced pressure to approximately three-fourths of its original volume and cooled in a dry-ice acetone bath under a stream of dry nitrogen. An equal volume of sodium-dried, low boiling petroleum ether, previously taken to the cold bath temperature, was added to the toluene solution. Soft, yellow crystals separated which were washed with the cold petroleum ether, and placed immediately in a desiccator under nitrogen and stored in a dry-ice chest.

The reaction was run in a number of media, including polar solvents such as ethanol and acetone, and in aliphatic and aromatic hydrocarbons. Sodium-dried, redistilled toluene possessed the most desirable properties. Similarly, low boiling petroleum ether was found to be best suited as a recrystallizing solvent. The recrystallization process itself appeared to catalyze the decomposition of these compounds. The gray coloration which was observed following recrystallization of the compounds was undoubtedly due to free tellurium formation.

The melting points and analytical data pertinent to this and the other phosphines prepared are given in Table 1.

TABLE 1

PHOSPHINE TELLURIDES

Derivative	*Melting point*	*Percent composition*		*Molecular weight*	
		Calcd.	*Found*	*Calcd.*	*Found*
Triethyl-	76.0– 78.0	C 29.32	29.40	245.6	[a]
		H 6.15	6.14		
		P 12.63	12.48		
Tri-*n*-propyl-	41.0– 42.0	C 37.55	37.56	287.8	[a]
		H 7.35	7.34		
		P 10.78	10.01		
Tri-*n*-butyl-	35.0– 35.5	C 43.69	43.88	329.9	343 ± 5
		H 8.25	8.24		
		P 9.39	9.62		
Tricyclohexyl-	184.0–187.0	C 52.98	53.09	408.1	410 ± 5
		H 8.15	8.14		
		P 7.59	7.49		
Phenyldi-*n*-propyl-[b]	67.0– 71.0	C 44.78	44.82	321.9	[a]
		H 5.95	5.91		
		P 9.62	9.67		
Phenyldi-*n*-butyl-	51.7– 53.5	C 48.05	48.06	349.9	[a]
		H 6.63	6.65		
		P 8.85	8.84		

[a] Not determined because of insufficient solubility and/or decomposition in solution. [b] Washed with *n*-heptane at dry-ice acetone temperature to remove excess, unreacted phosphine.

Solubility determinations

A three-necked flask was equipped with a sealed, mechanically driven teflon stirrer, reflux condenser and a thermometer which was immersed into the solution containing a weighed quantity (*ca.* 0.1 mole) of the phosphine in 500 ml of dry, redistilled toluene. A weighed quantity of tellurium powder (sufficient to assure an excess at equilibrium) was then added. The mixture was stirred at the desired temperature until equilibrium was reached, as evidenced by the constant weight of the residual tellurium powder. Three and one-half hours were found to be adequate.

The reaction mixture was poured as rapidly as possible* into a previously tared, fritted glass filter. The separated, unreacted tellurium powder was washed with ethanol and acetone and air-dried to constant weight. The number of moles of tellurium which had dissolved per mole of phosphine, which we shall call "percent solubility", may be defined as follows:

$$\frac{\text{moles Te dissolved}}{\text{moles phosphine}} \times 100.$$

In Table 2 the "percent solubility", as observed for nine phosphines at three different temperatures, is given.

TABLE 2

SOLUBILITY OF TELLURIUM IN VARIOUS PHOSPHINES

Phosphine	*Percent solubility*		
	25°	*50°*	*110°*
Phenyldimethyl-	20.40 ± 0.81	17.35 ± 0.29	16.69 ± 1.23
Phenyldiethyl-	48.66 ± 6.23	64.28 ± 1.80	47.82 ± 1.01
Phenyldi-*n*-propyl-	5.00 ± 0.09	4.17 ± 0.06	4.15 ± 0.40
Phenyldi-*n*-butyl-	9.26 ± 0.10	8.56 ± 0.14	9.10 ± 0.43
Diphenylmethyl-	3.48 ± 0.15	3.56 ± 0.12	4.06 ± 0.04
Diphenylethyl-	5.53 ± 0.22	5.65 ± 0.14	5.70 ± 0.75
Diphenyl-*n*-propyl-	3.47 ± 0.30	4.01 ± 0.92	3.62 ± 0.07
Diphenyl-*n*-butyl	2.25 ± 0.18	4.18 ± 0.25	3.54 ± 0.11
Triphenyl-	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00

RESULTS AND DISCUSSION

The six compounds which have been prepared represent all of the known phosphine tellurides. The yields of these compounds, based upon the amount of phosphine used, ranged from as low as five percent in the case of the phenyldi-*n*-propyl compound to as high as 45 percent in the case of the triethyl compound. In the other cases it ranged from 10–25 %. It should be remembered that in all cases, excess unreacted tellurium was present prior to separation of the compound.

The compounds, when they crystallized directly from the filtrate that separated from the reaction mixture, possessed a pale, golden yellow color, and analysis, *e.g.*, in the case of the tri-*n*-butyl derivative, indicated that they were stoichiometrically pure. When stored in an evacuated desiccator over anhydrous magnesium perchlorate at dry-ice temperature, they had acquired only a very pale gray coloration after two months' time. Exposure to air or even relatively gentle warming in solution brought about some decomposition and separation of tellurium metal. Hence, recrystallization of these compounds actually causes some decomposition. However, in no case was this decomposition sufficient to result in detectable changes in the analytical results.

In many cases, warming of solutions in saturated hydrocarbon solvents resulted in the formation of very even, shiny tellurium mirrors on the surfaces of the glass containers. Solutions in acetone, alcohol, or cyclohexane yielded a deposit of decomposition products heavily contaminated with tellurium metal.

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* The filtering procedure was greatly facilitated by adding to the reaction flask a fourth neck beneath and perpendicular to the center joint at a slightly inclined angle.

Because it was not possible to isolate certain derivatives, *e.g.*, from the reaction of phenyldiethylphosphine with tellurium, the preparation of these derivatives was attempted by passing gaseous hydrogen telluride through a suspension of the phosphine dibromide according to the following equation:

$$H_2Te + R_3PBr_2 \longrightarrow 2HBr + R_3PTe.$$

All such efforts were very unsuccessful; only large amounts of tellurium contaminated the reaction system without any apparent formation of the phosphine telluride.

Because of the lack of success in isolating tellurides which, based upon structural analogy with those already isolated, were expected to form, the solubility of tellurium in a number of phosphines was determined. The results of these determinations are shown in Table 2. It is to be noted that the solubility of tellurium in the various phosphines parallels their chemical reactivity, *i.e.*, the solubility decreases as the nucleophilic character of the phosphine decreases.

In order to learn something about the phosphorus–tellurium bonding, it would be desirable to investigate, among other things, the infrared spectra of these molecules, especially the location and nature of the fundamental P–Te stretching frequency. The force constant and frequency of an isolated P–Te bond can be estimated[3] and the values obtained are 1.6×10^5 dyne cm^{-1} and 331 cm^{-1}, or 3.2×10^5 dyne cm^{-1} and 472 cm^{-1} for a "pure" single bond and double bond, respectively. We have begun a preliminary search for this vibration, but this effort has been seriously complicated by the decomposition of the sample. This difficulty manifests itself primarily in the formation of a highly reflecting tellurium mirror on the interior walls of the cell. However, this effort is continuing and with the aid of different sample techniques it should be possible to locate this vibration.

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SUMMARY

The reaction of elemental tellurium with various alkyl- and arylalkylphosphines was investigated. Six phosphines tellurides were isolated as pure crystalline solids. The solubility of tellurium was determined in solutions of seven other phosphines whose tellurides were not isolated. Except in the case of triphenylphosphine, in which tellurium was completely insoluble, solubility studies indicated that from 0.3 to 0.65 moles of tellurium were dissolved per mole of phosphine.

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