*Journal of Organometallic Chemistry*, 190 (1980) 277—288

# THE REACTIONS OF SELENIUM TETRACHLORIDE AND TELLURIUM TETRACHLORIDE WITH SOME TRIVALENT ARYL ORGANOMETALLIC HALIDES

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(Received November 6th, 1979)

## Summary

The reactions of several trivalent organometallic aryl compounds with $TeCl_4$ and $SeCl_4$ were investigated. When diphenylboron bromide was treated with an equimolar quantity of tellurium tetrachloride in toluene, the phenyltellurium trihalide $C_6H_5TeBr_{1.3}Cl_{1.7}$ was obtained. The presence of the mixed halogens on tellurium can be explained in terms of a Lewis acid—base reaction between the boron and tellurium compounds. The reaction of diphenylboron bromide with selenium tetrachloride in toluene, produced mixed triarylselenonium chlorides. The presence of substituted toluene molecules in the product is attributed to the reaction of selenium tetrachloride with toluene in the presence of the Lewis acid, boron trihalide. The reaction of triphenylaluminum with tellurium tetrachloride was found to produce triphenyl telluronium chloride. Both diphenylchloroarsine and diphenylchlorophosphine were oxidized from $M^{III}$ to $M^{V}$ by either selenium or tellurium tetrachloride. The products were isolated as diphenylarsinic acid and diphenylphosphinic acid, respectively.

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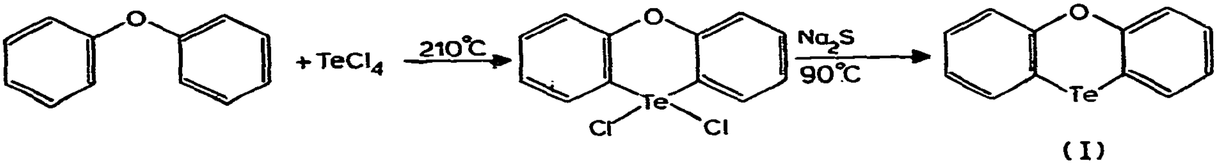
## Introduction

Phenoxatellurine (I) prepared by the reduction of the reaction product between diphenylether and tellurium tetrachloride (Scheme 1) [1] exhibits interesting donor properties in charge-transfer complexes [2].

SCHEME 1



(I)

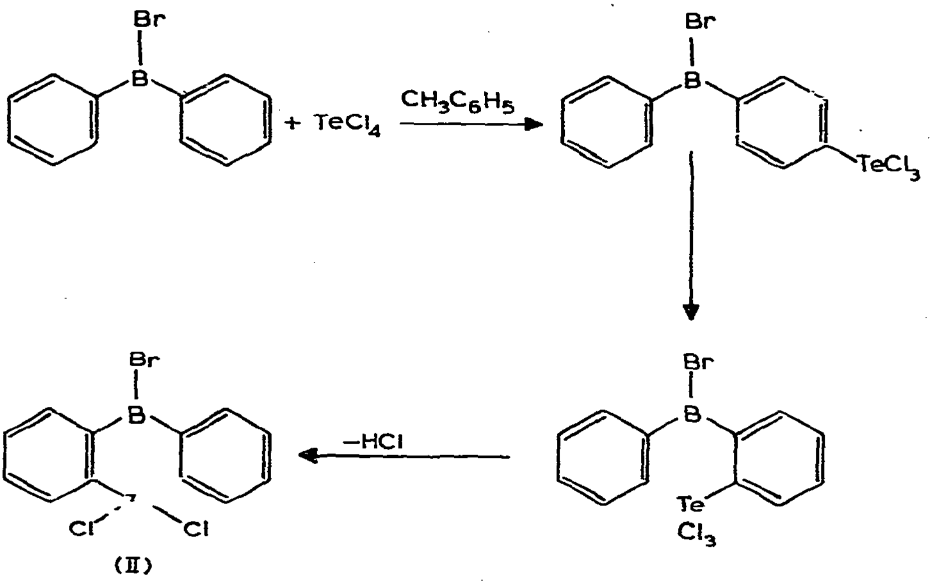
If the oxygen atom of phenoxatellurine were replaced by an electron deficient atom such as boron, this would effect a situation in which six electrons would be present in the central ring. If these electrons were delocalized, this system would satisfy the Hückel $4n + 2$ rule for aromaticity. If this occurs, the central ring may be aromatic and therefore planar. Such a compound may exhibit the donor properties of phenoxatellurine as well as the desired geometry to form a complex with 7,7,8,8-tetracyanoquinodimethane [3] which might, in its crystal structure, possess the desired segregated donor and acceptor stacked structure which is observed for the complex which forms between tetrathiafulvalene and 7,7,8,8-tetracyanoquinodimethane [4]. Attempts to prepare such compounds caused us to investigate the reaction between the tetrachlorides of tellurium and selenium with various aryl, trivalent, organometallic compounds.

## Results and discussion

The attempted syntheses of analogues of phenoxatellurine and phenoxaselenine in which oxygen is replaced by metal atoms such as boron, aluminum, phosphorus, or arsenic were disappointing in that none of the desired products was synthesized. However, a number of interesting observations and results were obtained in the study of the reactions used in the attempted syntheses.

The reaction between equimolar quantities of diphenylboron bromide and tellurium tetrachloride in toluene was performed to determine whether the boron-tellurium containing heterocycle(II) would be produced by electrophilic aromatic substitution of $TeCl_3^+$ onto one of the aromatic rings of diphenylboron bromide followed by subsequent intramolecular condensation in which a molecule of hydrogen chloride is lost. This anticipated reaction sequence is depicted in Scheme 2.

SCHEME 2



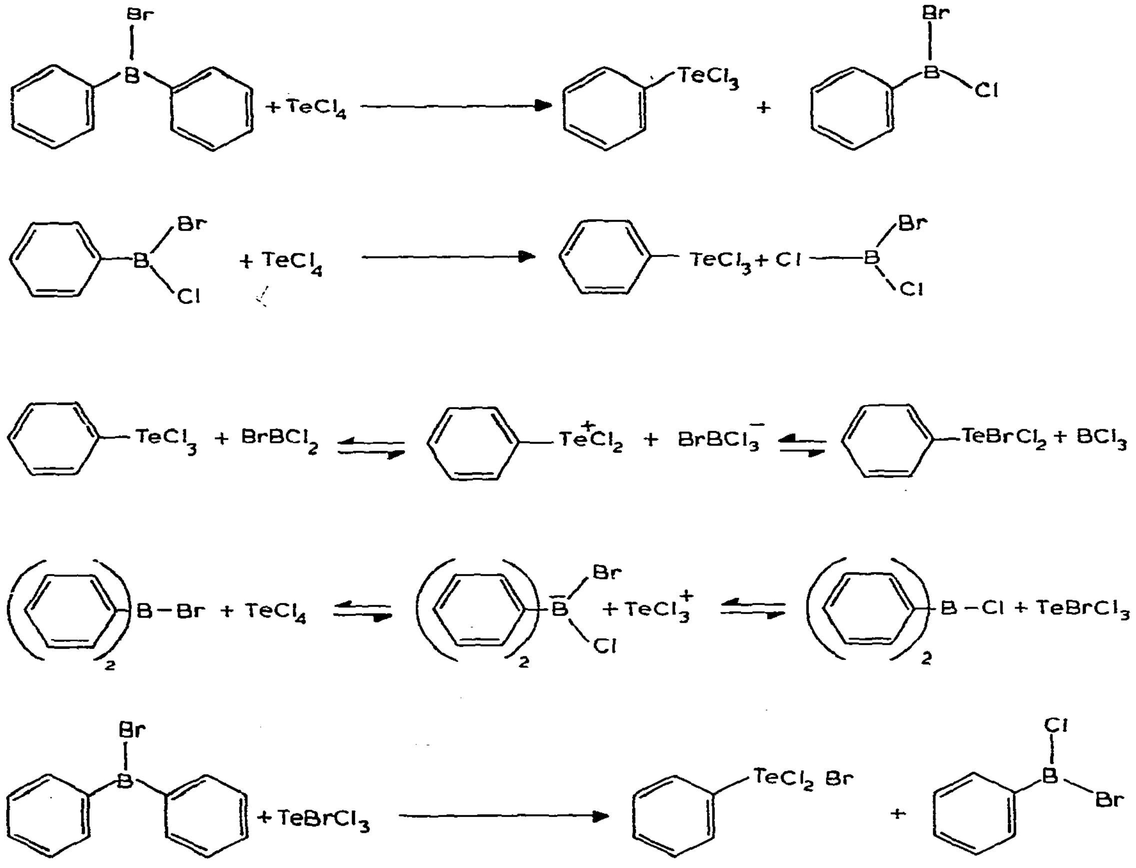
(II)

However, this did not occur. The reaction product that was formed crystallized slowly from benzene in the form of olive-green crystals. Chemical analysis of the crystals showed that bromine, chlorine and tellurium were present, but that boron was absent. Obviously, electrophilic substitution on the ring did not occur. Instead the B—C bond was broken with the formation of a Te—C bond. The product was identified by single crystal X-ray analysis as the phenyl tellurium trihalide $C_6H_5TeBr_{1.3}Cl_{1.7}$ [5]. The mass spectrum of the compound showed fragment ions of all four possible phenyl tellurium trihalides with the isotopic distribution expected for tellurium trihalides [6,7].

The presence of the mixed halogens on tellurium can be explained in terms of a Lewis acid—base reaction between the boron and tellurium compounds. Probable reactions which occurred are shown in Scheme 3. This is supported by the observation of Paul, Paul and Malhotra [8] who reported the formation of a complex between $BCl_3$ and $TeCl_4$.

Related reactions of $TeCl_4$ with two equivalents of $MAr_2Cl$ (M = Tl, In, and Ge; Ar = Ph, *p*-tolyl) provides a convenient method for the preparation of aryl tellurium chlorides by the cleavage of In—Ar, Tl—Ar, and Ge—Ar bonds [9].

SCHEME 3



A series of reactions was set up in which diphenylboron bromide was allowed to react with varying amounts of tellurium tetrachloride. The experimental details are given in Table 1. In this sequence of reactions, it was observed that as the amount of tellurium tetrachloride used is increased, the chlorine content of the phenyl tellurium trihalide is increased. This observation is based upon the chemical analyses for bromine and chlorine.

In addition, the reaction of triphenylboron with three molar equivalents of tellurium tetrachloride produced pure phenyl tellurium trichloride, as expected. Phenyl tellurium tribromide was independently produced by reaction of diphenyl ditelluride with bromine in chloroform [10,12]. The measured densities of the different phenyl tellurium trihalides were observed to increase as the bromine content of the trihalide was increased. This relationship may be linear, but because of the difficulties involved in obtaining reliable bromine analyses in the presence of chlorine, this hypothesis could not be tested quantitatively in this study.

The reaction of diphenylboron bromide with a two molar equivalent of selenium tetrachloride in toluene was performed with the expectation of similar results. The product which was obtained was impure, presumably because it was a mixture of triarylselenomium chlorides with some borid acid. Evidence to support this conclusion was obtained from the mass spectrum of the product. The mass spectrum showed the presence of boric acid as well as the fragments expected for the facile thermal decomposition of a triarylselenonium halide [12] within the probe of the mass spectrometer. This thermal decomposition of the triarylselenonium halide occurs with the formation of diaryl selenides and aryl halides [12] as shown in Scheme 4.

SCHEME 4

$$Ar_3Se^+, X^- \rightarrow Ar_2Se + ArX$$

$$Ar = C_6H_5^-, CH_3C_6H_4^-$$

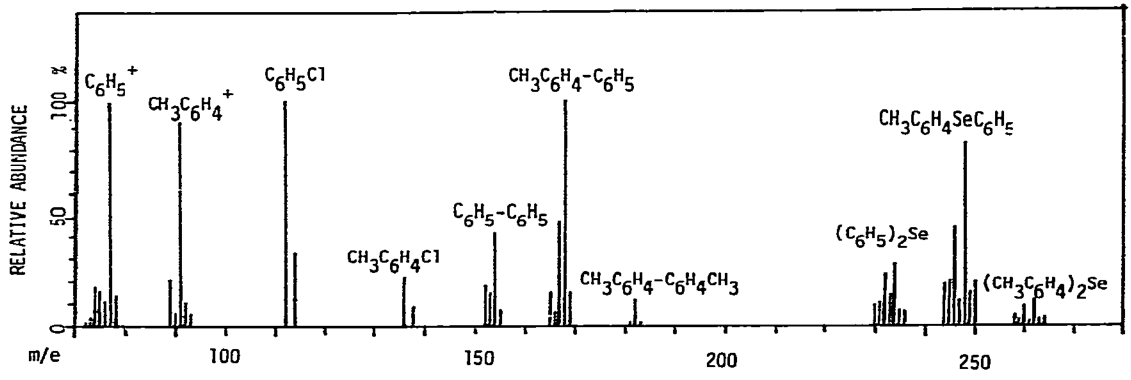
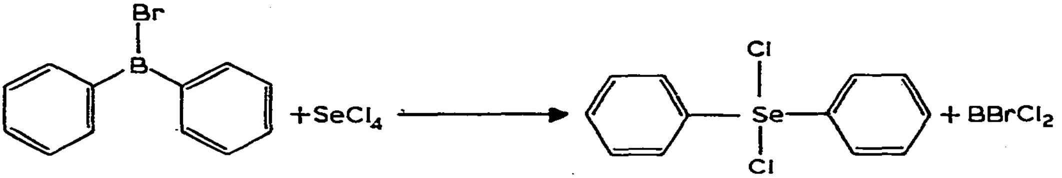


Fig. 1. The mass spectrum of the reaction product from the reaction of diphenylboron bromide with selenium tetrachloride. Values of *m/e* below 70 are excluded.

Ions with *m/e* ratios corresponding to the molecular ions for $(C_6H_5)_2Se$, $(CH_3{-}C_6H_4)_2Se$, $CH_3{-}C_6H_4SeC_6H_5$, $C_6H_5Cl$, and $CH_3C_6H_4Cl$ were all present in the mass spectra with the isotopic distribution expected for such compounds [6]. The mass spectra for the reaction product of diphenylboron bromide with selenium tetrachloride is shown in Figure 1. There is no evidence of the molecular ions, $C_6H_5Br$ or $CH_3C_6H_4Br$, indicating the presence of triarylselenonium chloride only.

The sequence of reactions which lead to the formation of triarylselenonium chloride obviously involved interaction of the reagents with the toluene solvent. The initial reaction which probably occurs is the reaction of diphenylboron bromide with selenium tetrachloride to yield diphenyldichloroselenium and $BBrCl_2$ (Scheme 5). It has been shown that diaryldichloroseleniums, in the presence of the Lewis acid, $AlCl_3$ and an aromatic solvent, react with the solvent to form triarylselenonium chlorides (Scheme 6) [13]. This interaction is similar to what may have occurred as a result of the reaction of diphenyldichloroselenium with toluene in the presence of the Lewis base.

SCHEME 5



SCHEME 6

$$Ar_2SeCl_2 + ArH \xrightarrow{AlCl_3} Ar_3Se^+, Cl^-$$

$$(C_6H_5)_2SeCl_2 + CH_3C_6H_5 \xrightarrow{BBrCl_2} (C_6H_5)_2(C_6H_4{-}CH_3)\,Se^+, Cl^-$$

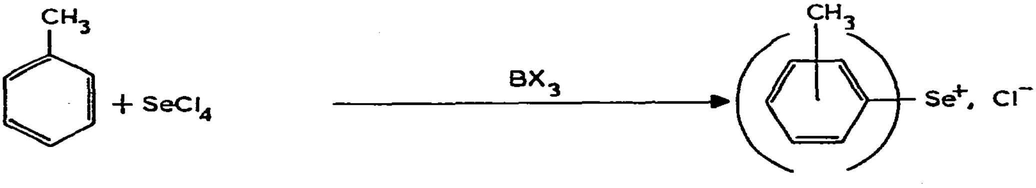
Additionally, it has been reported [14] that aromatic hydrocarbons react with selenium tetrachloride in the presence of the Lewis acid, $AlCl_3$, to form triarylselenonium chlorides (Scheme 7).

SCHEME 7

$$3\ ArH + SeCl_4 \xrightarrow{AlCl_3} Ar_3Se^+, Cl^- + 3\ HCl$$

This observation should be analogous to the reaction of toluene with $SeCl_4$ in the presence of the Lewis acid boron trihalide (Scheme 8) to give the tritolylselenonium chloride (III).

SCHEME 8



(III)

All of these reactions would account for the observation of the molecular ions for $(C_6H_5)_2Se$, $(CH_3{-}C_6H_4)_2Se$, $CH_3C_6H_4SeC_6H_5$, $C_6H_5Cl$, and $CH_3{-}C_6H_4Cl$. The presence of triphenylselenonium chloride in the reaction mixture is not precluded. However its formation cannot be easily explained from the data available, and its formation is unlikely. The triarylselenonium halides formed are probably $(C_6H_5)_2(CH_3{-}C_6H_4)Se^+, Cl^-$ and $(CH_3{-}C_6H_4)_3Se^+, Cl^-$. These two triarylselenonium chlorides would, upon thermal decomposition, yield all of the observed compounds.

The reaction of tellurium tetrachloride with triphenylaluminum is especially interesting in that triphenyl telluronium chloride was isolated as the product. This observation is probably best explained by the following sequence of reactions (Scheme 9).

SCHEME 9

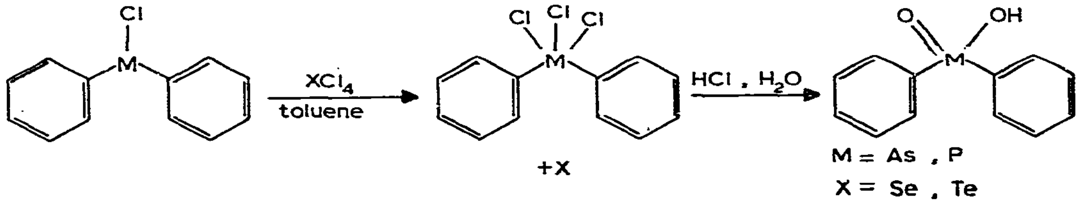
$$\begin{tikzcd}
Ph_3Al + TeCl_4 \arrow[r] & Ph_3AlCl^- + TeCl_3^+ \arrow[d] \\
PhTeCl_2^+ + Ph_2AlCl_2^- \arrow[d] & PhTeCl_3 + Ph_2AlCl \arrow[l] \\
Ph_2TeCl_2 + PhAlCl_2 \arrow[r] & Ph_2TeCl^+ + PhAlCl_3^- \arrow[d] \\
Ph_3Te^+ \cdot AlCl_4^- \arrow[dr, "H_2O"', "100^\circ C"] & Ph_3TeCl + AlCl_3 \arrow[l] \\
 & Ph_3Te^+, Cl^- + Al(OH)_3
\end{tikzcd}$$

What probably occurs is the initial formation of a $Ph_3Al \cdot TeCl_4$ complex (which is similar to observations by Coates [15]), which undergoes the reactions in Scheme 9. It is important to note that the product obtained was pure triphenyltelluronium chloride. There was no solvent interaction as in the case of diphenylboron bromide and selenium tetrachloride.

The preparation and characterization of the adduct $TeCl_3^+ \cdot AlCl_4^-$, which is similar to the intermediate initially formed in the reaction of $Ph_3Al$ with $TeCl_4$ has been described by Beattie and Chudzynska [16]. This adduct has been shown to be an effective reagent for the electrophilic aromatic substitution of $TeCl_4$ on to the aromatic ring of benzene (benzene is inert to $TeCl_4$ alone) [17].

The reactions of diphenylchlorophosphine and diphenylchloroarsine with tellurium tetrachloride and selenium tetrachloride involved an oxidation—reduction reaction in which diphenylchlorophosphine and diphenylchloroarsine were oxidized from the $M^{III}$ to $M^{V}$ oxidation states as described in Scheme 10.

SCHEME 10



In those reactions in which diphenylchlorophosphine was used, the product was isolated as diphenylphosphinic acid. This product resulted from the hydrolysis of diphenyltrichlorophosphorane, which was probably formed initially. In a similar manner, diphenyltrichloroarsine is probably formed initially and hydrolyzed to diphenylarsinic acid (isolated as the hydrochloride). In both of these reactions, elemental selenium or tellurium was precipitated from the reaction mixture. These observations parallel those of Berry et al. [18] who observed that triphenylarsine and triphenylphosphine are oxidized from $M^{III}$ to $M^{V}$ by $TeCl_4$ in benzene and isolated after hydrolysis of the dichlorides, as triphenylphosphine oxide and triphenylarsine oxide hydrochloride.

## Experimental section

All reactions were carried out in flame-dried glassware under purified nitrogen using standard techniques [19]. $^1H$ NMR spectra were recorded on a Varian T-60 NMR spectrometer. $^{13}C$ NMR spectra were recorded on a Jeol Model JNM-PS-100 high resolution NMR spectrometer equipped with a Nicolet 1080 E data processing system in the T-1 mode. A sweep width of 5617.977 Hz (224.4 ppm), a sweep frequency of 25.0344 MHz (obs), and an irradiating frequency of 99.5388 MHz at 10 watts power were used. $CDCl_3$ was the source of an internal deuterium lock. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Mass spectra were measured by G.M. Gable and R.D. Grigsby who recorded them on a CEC21-110B mass spectrometer employing an accelerating voltage of 8000 V. The molecules were bombarded with 70 eV electrons. The nominal masses were determined by reference to a perfluorokerosine standard. Melting points were taken on a Büchi SMP-20 melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

Diphenylboron bromide and $SeCl_4$ were purchased from Alfa Corporation and used without further purification. Triphenylboron, diphenylchloroarsine and diphenylchlorophosphine were purchased from Pfaltz and Bauer, Inc. and were used without further purification. Triphenylaluminum was purchased from Organometallics Inc. and was used without purification.

All other reagents and solvents were purchased from commercial sources as reagent grade chemicals.

### *Reaction of diphenylboron bromide with tellurium tetrachloride*

A 100-ml round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and rubber septum was flushed with nitrogen and flame-dried. To the flask were added 4.51 g (16.75 mmol) of tellurium tetrachloride and 60 ml of anhydrous toluene. Diphenylboron bromide (3.0 ml, 4.1 g, 16.75 mmol) was added dropwise via syringe. After addition of the diphenylboron bromide, the formation of a precipitate was observed. The mixture was then refluxed for 6 h and cooled. Anhydrous ether (25 ml) was added to the reaction mixture, which then was filtered. The filtered precipitate was washed with 150 ml of anhy-

TABLE 1

REACTIONS OF DIPHENYLBORON BROMIDE WITH TELLURIUM TETRACHLORIDE

| Reaction | Amount of $(C_6H_5)_2BBr$ | Amount of $TeCl_4$ | Ratio $(C_6H_5)_2BBr/TeCl_4$ | Amount of Product | m.p. (°C) | % Cl | % Br | Density (g/cm$^3$) |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.1g, 16.75 mmol | 2.26g, 8.30 mmol | 1/0.5 | 2.85g | 219–222 | 6.19 | 37.3 | 2.8084 |
| 2 | 4.1g, 16.75 mmol | 4.51g, 16.75 mmol | 1/1.0 | 5.35g | 218–221 | 20.1 | 22.3 | 2.5811 |
| 3 | 4.1g, 16.75 mmol | 6.77g, 25.13 mmol | 1/1.5 | 7.65g | 217–220 | 21.6 | 15.3 | 2.4739 |
| 4 | 4.1g, 16.75 mmol | 9.03g, 33.51 mmol | 1/2.0 | 6.60g | 214–217 | 25.7 | 12.6 | 2.4162 |

drous ether to remove unreacted $TeCl_4$ and diphenylboron bromide as well as side products such as boron trihalides and boric acid. There was obtained 5.35 g of a pale yellow-green solid; m.p. 218—221°C. The mass spectrum shows fragment ions of all four possible phenyl tellurium trihalides with the correct isotopic distributions expected for tellurium halides [6,7]; *m/e* 367 (4.7), 365 (10.9), 363 (12.5), 362 (3.1), 361 (10.9), 360 (4.7), 359 (4.7%), isotopic cluster for $C_6H_5TeBr_2^+$; 325 (12.5), 323 (45.3), 321 (68.8), 319 (50.0), 318 (15.6), 317 (29.7), 316 (10.9), 315 (10.9%), isotopic cluster for $C_6H_5TeBrCl^+$; 279 (48.4), 277 (100), 275 (87.5), 274 (14.1), 273 (48.3), 272 (20.3), 271 (15.6%), isotopic cluster for $C_6H_5TeCl_2^+$. Anal. Found: C, 19.90; H, 1.40; Cl, 14.01; Br, 29.72, Te, 32.52%. The product was identified as $C_6H_5TeBr_{1.3}Cl_{1.7}$ by single crystal X-ray analysis [5]; $\rho = 2.6520$ g/cm$^3$.

A series of four reactions were set up as described above. The amount of diphenylboron bromide (4.1 g, 33.5 mmol) was kept constant, while the quantity of tellurium tetrachloride was varied. The reactions were refluxed 4 h and worked up in the manner described. Table 1 shows the amounts of reagent used, the ratio of diphenylboron bromide to tellurium tetrachloride, the amounts of products, the m.p. range of products, the densities, and the amount of Cl and Br found. From the table, it is apparent that the chlorine content of the product increases as more tellurium tetrachloride is used.

### *Phenyl tellurium trichloride*

In a 25-ml round-bottomed flask equipped with a magnetic stirrer and rubber septum were placed 1.5 g (6.204 mmol) of triphenylboron and 3.1527 g (18.611 mmol) of tellurium tetrachloride. Toluene (10 ml) was added as the solvent and the reaction was vented with a bubbler. The reaction was stirred for 24 h at 50°C after which time it was cooled, filtered, and washed with 100 ml of anhydrous ether to yield 2.56 g (8.25 mmol, 44.3%) of a white solid. The product was recrystallized in the form of colorless crystals of phenyl tellurium trichloride; m.p. 217—220°C (lit. [20] m.p. 215—218°C); IR(KBr) 1470, 1425, 1042, 988, 720(s), and 670 cm$^{-1}$. Anal. Found: C, 22.76; H, 1.65; Cl, 34.1. $C_6H_5TeCl_3$ calcd.: C, 23.15; H, 1.61; Cl, 34.20%. $\rho = 2.2873$ g/cm$^3$.

### *Diphenyl ditelluride*

In a 100-ml round-bottomed flask were placed 4.0 g (12.86 mmol) of phenyl tellurium trichloride and 5.0 g (20.8 mmol) of $Na_2S \cdot 9\ H_2O$. The flask was heated to 90°C in a water bath for 0.5 h after which time it was cooled, and the contents of the flask were filtered. The precipitate was washed with 100 ml of distilled water to yield 2.5 g (6.11 mmol, 95.1%) of crude diphenyl ditelluride, which was recrystallized from methanol to leave bright orange crystals; m p. 66°C (lit. [6] m.p. 66—67°C). The mass spectrum showed the isotopic cluster expected for $(C_6H_5Te)_2^{+\cdot}$ as reported in the literature for $Te_2$ compounds and diphenyl ditelluride [6].

### *Phenyl tellurium tribromide*

Following the general procedure for making organyl tellurium trihalides [18,19], 2.0 g (4.89 mmol) of diphenyl ditelluride was dissolved in 40 ml of chloroform. Bromine was added dropwise via pipet until there was no additional precipitation of triphenyl tellurium tribromide. The product was collected by filtration and washed with 100 ml of chloroform to yield 3.9 g (8.77 mmol, 87.7%) of yellow phenyl tellurium tribromide. Recrystallization from methanol afforded crystals; m.p. 239—241° C; IR(KBr) 1430, 1045, 986, 720(s), and 677 cm$^{-1}$. Anal. found: 53.9. C$_6$H$_5$TeBr$_3$ calcd.: Br, 53.9%. $\rho$ = 2.9550 g/cm$^3$.

*Reaction of diphenylboron bromide with selenium tetrachloride*

In a 100-ml round-bottomed flask equipped with a magnetic stirrer and rubber septum was placed 7.4 g (33.51 mmol) of selenium tetrachloride. Toluene (40 ml) was added followed by the dropwise addition (via syringe) of 3.0 ml (4.1 g, 16.75 mmol) of diphenylboron bromide. Hydrogen chloride was evolved upon addition of the diphenylboron bromide and it was vented through a bubbler. The yellow precipitate which formed was collected by filtration and washed with anhydrous ether to yield 1.20 g of a light yellow compound; m.p. 130—161° (d). The compound was not pure and contained some boric acid as determined by mass spectroscopy. Mass spectroscopy showed fragmentations for (Ar)$_2$Se; *m/e* 262 (10), for (CH$_3$C$_6$H$_4$)$_2{}^{80}$Se; 248 (70), for CH$_3$-C$_6$H$_4{}^{80}$Se$_6$H$_5$; 234 (35), for (C$_6$H$_5$)$_2{}^{80}$Se; 126 (20), for CH$_3$C$_6$H$_4{}^{35}$Cl; 112 (100%), for C$_6$H$_5{}^{35}$Cl. The product was a mixed triarylselenonium chloride which thermally decomposed [12] within the mass spectrometer. All selenium and chloride containing fragment ions were present in the expected isotopic ratios [6,7].

*Reaction of triphenylaluminum with tellurium tetrachloride*

A 500-ml round-bottomed flask equipped with a magnetic stirrer, pressure equalizing addition funnel, and rubber septum was flushed with nitrogen and flame-dried. To the flask were added 15.66 g (58.14 mmol) of tellurium tetrachloride and 300 ml of anhydrous toluene. To the addition funnel were added 5.0 g (19.38 mmol) of triphenylaluminum in 50 ml of anhydrous toluene. The reaction flask was cooled in an ice-water bath. The triphenylaluminum-toluene solution was added dropwise over a period of 2 h after which time the reaction mixture was rapidly filtered. The light yellow precipitate which was collected was rapidly washed with 300 ml of anhydrous ether and dried; m.p. >300° C; IR(KBr) 1420, 1170, 1045(w), 985, 840(w), 735(s), and 680 cm$^{-1}$. This compound, which was insoluble in most organic solvents, was added to 250 ml of water and heated. As the water was heated, the compound went into solution. A small amount of white precipitate [Al(OH)$_3$] remaining in the hot water was removed by filtration. As the filtrate was cooled, white crystalline needles formed. The crystals were collected by filtration and air dried to yield 3.8 g (9.64 mmol, 49.7%) of triphenyl tellurium chloride; m.p. 245—246° C (lit. [21] m.p. 244—245° C); IR(KBr) 3500(b, m), 3050, 1570, 1430, 1176(w), 1062, 1015(w), 992, 733(vs), and 685 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ (ppm) 7.88 (m, 2H), 7.44 (m, 3H). Anal. found: C, 54.31; H, 3.81. C$_{18}$H$_{15}$TeCl calcd.: C, 54.81; H, 3.81%.

*Reaction of diphenylchloroarsine with selenium tetrachloride*

In a dried 100-ml round-bottomed flask equipped with a magnetic stirrer was placed 2.08 g (2.45 mmol) of selenium tetrachloride. The flask was fitted with a rubber septum and flushed with nitrogen. To the flask was then added 40 ml of anhydrous toluene followed by the dropwise addition (via syringe) of 2.5 g (9.45 mmol) of diphenylchloroarsine. The reaction turned reddish-brown due to deposition of elemental selenium. The reaction mixture was stirred for 2 h. Ether (50 ml) was added to the reaction mixture which was then filtered to remove elemental selenium. The filtrate was washed with distilled water (50 ml), dried ($Na_2SO_4$) and evaporated to leave 2.6 g (8.71 mmol, 92.2%) of rose-colored crystals. The crystals were recrystallized from benzene to yield colorless crystals; m.p. 131—133° C (lit. [22] m.p. 133° C), which were identified as diphenylarsinic acid hydrochloride. IR(KBr) 2520(very broad), 2270(b), 1430, 1330(w), 1310(w), 1180, 1080, 990(w), 783, 765, 730, 670, 456, and 357 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ (ppm) 8.12 (s, 1H), 7.98 (m, 2H), 7.73 (m, 3H). The mass spectrum shows a $M^{+\cdot}$ for diphenylarsinic acid at 261 (50); 245 (65), for $C_{12}H_{10}AsO$; 229 (100), for $C_{12}H_{10}As$; 169 (50), for $C_6H_6AsO$; 154 (80), for $C_{12}H_{10}$; 152 (76), for $C_6H_5As$; 91 (45), for AsO. Anal. found: C, 48.71; H, 4.08; Cl, 12.87. $C_{12}H_{12}AsOCl$ calcd.: C, 48.25; H, 4.02; Cl, 12.70%.

### *Reaction of diphenylchloroarsine with tellurium tetrachloride*

Following the procedure described above, 2.45 g (9.45 mmol) of tellurium tetrachloride was treated with 2.5 g (9.45 mmol) of diphenylchloroarsine in 40 ml of toluene. Tellurium metal precipitated immediately indicating a reduction of $Te^{IV}$ to elemental Te. The reaction mixture was added to anhydrous ether (100 ml) and filtered to remove elemental tellurium (0.6 g, 4.7 mmol). The filtrate was evaporated to an oil which crystallized upon standing. The solid was recrystallized from $CHCl_3$ to yield 2.4 g (8.04 mmol, 85.1%) of diphenylarsinic acid hydrochloride; m.p. 132—133° C (lit. [22] m.p. 133°).

### *Reactions of diphenylchlorophosphine with tellurium tetrachloride*

Following the general procedure for the reaction of diphenylchloroarsine with selenium or tellurium tetrachloride, 4.0 ml (6.3 g, 28.6 mmol) of diphenylchlorophosphine was treated with 3.85 g (14.36 mmol) of tellurium tetrachloride in 50 ml of anhydrous toluene. Elemental tellurium, 1.6 g (12.5 mmol), was recovered by filtration. The product was recovered from the filtrate by hydrolysis with water, drying ($Na_2SO_4$), and evaporation to leave 5.9 g (27.1 mmol, 94.6%) of product, which was recrystallized from methanol to give diphenylphosphinic acid; m.p. 196—198° C (lit. [23] m.p. 197° C); IR(KBr) 2950(s), 1450, 1180, 1130, 756, 730(s), and 692 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) $\delta$ (ppm) 9.55 (broad s, 1H), 7.77 (broad m, 2H), 7.45 (m, 3H).

### *Reaction of diphenylchlorophosphine with selenium tetrachloride*

Following the same procedure used with tellurium tetrachloride, 4.0 ml (6.3 g, 28.6 mmol) of diphenylchlorophosphine was treated with 3.2 g (14.3 mmol) of selenium tetrachloride in 50 ml of anhydrous toluene. There was recovered 1.0 g (12.5 mmol, 96.2%) of diphenylphosphinic acid; m.p. 195—197° C (lit. [23] m.p. 197° C).

## Acknowledgement

We would like to express our gratitude to the Robert A. Welch Foundation and the Selenium-Tellurium Development Association for financial assistance in support of this research.

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