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REACTION OF ARYLSELENENYL BROMIDES AND 2-NAPHTHYLTELLURENYL IODIDE WITH TRIETHYLAMINE AND TRIVALENT PHOSPHORUS COMPOUNDS

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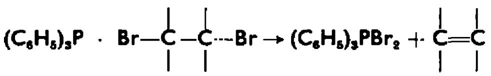
Abstract—Arylselenenyl bromides and 2-naphthyltellurenyl iodide are reduced by triphenylphosphine, triethylamine and tri-isopropyl phosphite giving the corresponding diselenides and ditelluride. The halogenated derivatives of the amine and phosphorus compounds were also characterized.

CARBON TETRAHALIDES are dehalogenated by using triphenylphosphine, yielding triphenyldihalophosphine and dihalomethylenetriphenylphosphorane.[1,2]

$$CX_4 + 2(C_6H_5)_3P \rightarrow (C_6H_5)_3PX_2 + (C_6H_5)_3P{=}CX_2$$
$$X{=}Cl,Br$$

vic-Dibromides have been similarly reduced to the corresponding olefins:[3]



$$(C_6H_5)_3P + Br{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Br \rightarrow (C_6H_5)_3PBr_2 + \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}}$$

Diaryltellurides also promote similar reductions.[4]

In the present paper the reactions of triphenylphosphine with arylselenenyl bromides and 2-naphthyltellurenyl iodide are discussed.

Triphenylphosphine reduces arylselenenyl bromides quantitatively to the corresponding diselenide and a brominated derivative of triphenylphosphine forms, which on treatment with water yield triphenylphosphine oxide.

$$(C_6H_5)_3P + 2ArSeBr \rightarrow Ar{-}Se{-}Se{-}Ar + (C_6H_5)_3PBr_2$$
$$(C_6H_5)_3PBr_2 + H_2O \rightarrow (C_6H_5)_3PO + 2HBr$$
$$Ar{=}C_6H_5{-},\quad 2,4\text{-}(NO_2)_2C_6H_3{-}$$

In the case of 2-naphthyltellurenyl iodide,* an unstable intermediate was isolated. The tellurium content of the crystalline yellow compound, containing iodine and

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* Prepared *in situ* from the ditelluride and iodine.[5]

[1] R. Rabinowitz and R. Marcus, *J. Amer. Chem. Soc.* **84**, 1312 (1962).

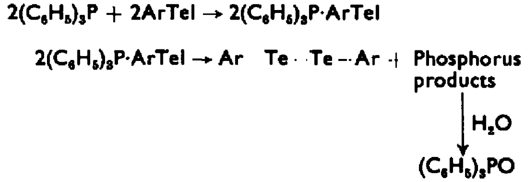
[2] F. Ramirez, N. Desai and N. McKelvie, *J. Amer. Chem. Soc.* **84**, 1745 (1962).

[3] C. C. Tung and A. J. Speziale, *J. Org. Chem.* **28**, 1521 (1963).

[4] M. Moura Campos, N. Petragnani and C. Thomé, *Tetrahedron Letters* No. 15, 5 (1960).

[5] G. Vicentini, E. Giesbrecht and L. R. M. Pitombo, *Chem. Ber.* **92**, 40 (1959).

phosphorus also, is consistent with an equimolar adduct of triphenylphosphine and 2-naphthyltellurenyl iodide. Until the structure of this adduct has been investigated, it may be mentioned that its formation requires a 100% excess of triphenylphosphine which can be recovered unchanged from the reaction mixture. Equivalent amounts of the reactants yield an indefinite pasty product which at room temperature in an open vessel, slowly changes, a brownish colour being produced. Attempts to crystallize this compound were unsuccessful and transformed it into the corresponding ditelluride. Triphenylphosphine oxide was isolated from the filtered solution, on addition of water, but when recrystallized in the presence of triphenylphosphine, the adduct separates without decomposition.



$$2(C_6H_5)_3P + 2ArTeI \rightarrow 2(C_6H_5)_3P\cdot ArTeI$$

$$2(C_6H_5)_3P\cdot ArTeI \rightarrow Ar-Te-Te-Ar + \text{Phosphorus products} \xrightarrow{H_2O} (C_6H_5)_3PO$$

This reaction was extended to triethylamine since it is known that tertiary amines react with halogens giving rise to dihalogen amines.[6,7] The formation of trialkylchloroammonium cation was reported by Ellis and Soper[8] during a kinetic study of the chlorination of tertiary amines.

In the reaction of triethylamine with arylselenenyl bromides, reduction occurs, affording the diselenide in almost quantitative yield when a 100% excess of the amine is used. Triethylammonium bromide was also formed in high yields "via" bromination of the ethyl groups (step 2) giving rise to hydrogen bromide through the protonization of the more basic triethylamine (step 3).[7,9]

$$(C_2H_5)_3N + 2ArSeBr \rightarrow Ar{-}Se{-}Se{-}Ar + (C_2H_5)_3NBr_2 \qquad (1)$$

$$(C_2H_5)_3NBr_2 \rightarrow (C_2H_5)_2NCHBr{-}CH_3 + HBr \qquad (2)$$

$$HBr + (C_2H_5)_3N \rightarrow (C_2H_5)_3N\cdot HBr \qquad (3)$$

The high yields of triethylammonium bromide in the bromination of the triethylamine in benzene solution agrees with Water's results.[9] In the reaction of triethylamine with 2-naphthyltellurenyl iodide, a small amount (14%) of triethylammonium iodide and an indefinite product containing tellurium and iodine were observed in addition to the expected ditelluride. The unknown product on treatment with aqueous sodium hydroxide produced free triethylamine.

It was also observed that, on treating triethylamine with iodine in organic solvents, a pasty dark residue separates without formation of triethylammonium iodide. Nagakura,[10,11] however reported the formation of a molecular triethylamine-iodine compound.

[6] A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **38**, 2161 (1905).

[7] H. Böhme and W. Krause, *Chem. Ber.* **84**, 170 (1951).

[8] A. J. Ellis and F. G. Soper, *J. Chem. Soc.* 1750 (1954).

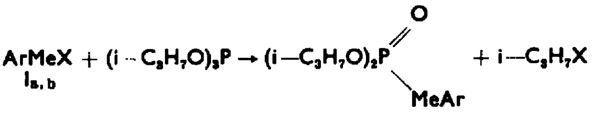
[9] C. W. Crane, J. Forrest, O. Stephenson and W. A. Waters, *J. Chem. Soc.* 827 (1946).

[10] S. Nagakura, *J. Amer. Chem. Soc.* **80**, 520 (1958).

[11] H. Tsubomura and S. Nagakura, *J. Chem. Phys.* **27**, 819 (1957).

In the reaction of tri-isopropylphosphite with arylselenenyl- and aryltellurenyl halides, two paths are possible:

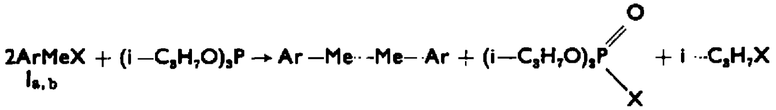
(a) An Arbuzov type of reaction as observed with sulphenyl chlorides[12] and trialkyl tin chlorides,[13] giving arylseleno- and aryltellurophosphonate:



$$\underset{I_{a,b}}{ArMeX} + (i-C_3H_7O)_3P \rightarrow (i-C_3H_7O)_2P(=O)MeAr + i-C_3H_7X$$

$I \begin{cases} a: Me{=}Se; & X{=}Br; & Ar{=}2,4\text{-}(NO_2)_2C_6H_3- \\ b: Me{=}Te; & X{=}I; & Ar{=}2-C_{10}H_7- \end{cases}$

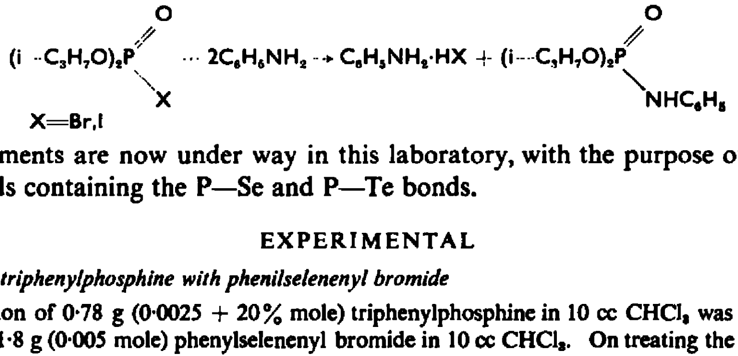
(b) A dehalogenation reaction to diselenide and ditelluride leading to di-isopropyl halogenophosphonate as observed with sulphuryl chloride[14] and halogens:[15,16]



$$\underset{I_{a,b}}{2ArMeX} + (i-C_3H_7O)_3P \rightarrow Ar-Me-Me-Ar + (i-C_3H_7O)_2P(=O)X + i-C_3H_7X$$

$I \begin{cases} a: Me{=}Se; & X{=}Br; & Ar{=}2,4\text{-}(NO_2)_2C_6H_3- \\ b: Me{=}Te; & X{=}I; & Ar{=}2\text{-}C_{10}H_7- \end{cases}$

The results obtained are in accordance with path (b) since diselenide and ditelluride were formed in good yield (a 100% excess of tri-isopropylphosphite was employed). The di-isopropyl halogenophosphonate was isolated and characterized as the known di-isopropyl N-phenylaminophosphonate[14]



$$(i-C_3H_7O)_2P(=O)X + 2C_6H_5NH_2 \rightarrow C_6H_5NH_2{\cdot}HX + (i-C_3H_7O)_2P(=O)NHC_6H_5$$

$X{=}Br, I$

Experiments are now under way in this laboratory, with the purpose of isolating compounds containing the P—Se and P—Te bonds.

EXPERIMENTAL

Reaction of triphenylphosphine with phenilselenenyl bromide

A solution of 0·78 g (0·0025 + 20% mole) triphenylphosphine in 10 cc $CHCl_3$ was added to a solution of 1·8 g (0·005 mole) phenylselenenyl bromide in 10 cc $CHCl_3$. On treating the pale yellow solution with pet. ether (50–70°) an orange oil separated. Decantation and evaporation of the solvent gave the diselenide as a yellow oil which crystallized on cooling (0·78 g, 100%) and on recrystallization from methanol gave yellowish needles m.p. 61–62° (in accord with lit.[17]). The orange oil, on contact with atmosphere liberated HBr, and on treatment with water, triphenylphosphine oxide was obtained 0·70 g (100%) which was crystallized from benzene and pet. ether (30–50°) m.p. 152°.

Reaction of triphenylphosphine with 2,4-dinitrophenylselenenyl bromide

A solution of 0·78 g (0·0025 mole + 20%) triphenylphosphine in 10 cc $CHCl_3$ was added to a solution of 1·63 g (0·005 mole) 2,4-dinitrophenylselenenyl bromide in 100 cc $CHCl_3$. The resulting

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[12] D. C. Morrison, *J. Amer. Chem. Soc.* **77**, 81 (1955).

[13] B. A. Arbuzov and A. N Pudovik, *J. Gen. Chem.* (*U.S.S.R.*) **17**, 2158 (1947); *Chem. Abstr.* 42 4522a (1948).

[14] A. C. Poshkus and J. E. Herwek, *J. Amer. Chem. Soc.* **79**, 6127 (1957).

[15] H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.* 380, 921 (1945).

[16] W. Garrard and G. J. Jeacocke, *J. Chem. Soc.* 3647 (1954).

[17] O. Behagel and H. Seibert, *Ber. Dtsch. Chem. Ges.* **65**, 815 (1932).

yellow crystalline precipitate of the diselenide 1·23 g (100%), was recrystallized from nitrobenzene and ethanol in yellow needles, m.p. 264–265° (in accord with lit.[18]). The filtered chloroformic solution was washed with small amounts of water, dried (Na_2SO_4), concentrated and treated with pet. ether (30–50°). By slow evaporation of the solvent triphenylphosphine oxide separates, 0·70 g (100%), m.p. 152°.

Reaction of triphenylphosphine with 2-naphthyltellurenyl iodide

A solution of 1·02 g (0·002 mole) di-2-naphthylditelluride and 2·10 g (0·008 mole) triphenylphosphine in 40 cc benzene was treated dropwise, while stirring mechanically, with a solution of 0·51 g (0·002 mole) I_2, in 40 cc benzene, yielding a yellow crystalline precipitate. After 2 hr the product was separated by filtration and washed with benzene. The solution was evaporated, the orange residue dissolved in ether and the small insoluble residue disregarded. After evaporation of ether, 0·90 g triphenylphosphine was recovered (95% of the excess employed). The yellow crystalline adduct 2·45 g (95%) melts with decomposition at 155–160°. The preparation was unsuccessful when a 100% excess of triphenylphosphine was not employed. A pasty brown product was obtained from which no definite substance could be isolated. In the same way, an unsatisfactory result was obtained treating a suspension of 2-naphthyltellurenyl iodide (1·52 g; 0·004 mole) in benzene with triphenylphosphine (2·10 g; 0·008 mole). The adduct (2·5 g) retains considerable amount of the starting iodide. Attempts for crystallization of the adduct was unsuccessful. It is insoluble in all cold usual organic solvents, and on treatment with boiling ethanol, benzene, chloroform, acetone, glacial acetic acid, decomposition slowly occurs giving ditelluride. The recrystallization was only possible when effected in a chloroform benzene mixture in the presence of equal amounts of triphenylphosphine. Found: Te, 19·02%; Calc. for $C_{28}H_{22}TeIP$: Te, 19·81%. The compound decomposes slowly acquiring a brownish colour.

Transformation of the adduct in ditelluride. 1·2 g (0·0019 mole) of the compound was treated with 50 cc boiling ethanol until complete solution. By cooling 0·30 g ditelluride (64%) was obtained. Red needles m.p. 120–122° (in accord. with lit.[5]). The filtered solution was concentrated and on adding small amounts of water, triphenylphosphine oxide separated 0·35 g (66%) m.p. 150–152°.

Reaction of triethylamine with phenylselenenyl bromide

A solution of 1·18 g (0·005 mole) phenylselenenyl bromide in 10 cc $CHCl_3$ was treated with 0·50 g (0·005 mole) triethylamine. The yellow solution was treated with pet. ether (50–70°). Triethylammonium bromide precipitated as colourless needles, 0·81 g (89%) m.p. 255°. The filtered solution was evaporated giving 0·70 g diselenide (90%). Recrystallized from methanol in yellowish needles, m.p. 61°.

Reaction of triethylamine with bromide

1·01 g (0·01 mole) triethylamine in 10 cc benzene was treated with 0·80 g (0·005 mole) Br_2. The solution was diluted with pet. ether giving colourless needles of triethylammonium bromide, 1·30 g (71%), m.p. 255°. Starting from equimolar amounts of the reagents, triethylammonium bromide was formed in 77% yield.

Reaction of triethylamine with 2,4-dinitrophenylselenenyl bromide

A solution of 0·98 g (0·003 mole) 2,4-dinitrophenylselenenyl bromide in 20 cc benzene was stirred with 0·30 g (0·003 mole) triethylamine. The heterogeneous crystalline precipitate was separated and extracted several times with ethanol. The yellow orange residue of diselenide 0·69 g (93%) was recrystallized from a mixture of nitrobenzene and ethanol in yellow needles, m.p. 264–265°. The ethanolic solution was evaporated, and the residue washed with benzene to give crystalline triethylammonium bromide, 0·40 g (73%), m.p., after recrystallization from ethanol, 255°.

Reaction of triethylamine with 2-naphthyltellurenyl iodide

A suspension of 0·95 g (0·0025 mole) 2-naphthyltellurenyl iodide in 25 cc benzene was stirred with 0·25 g (0·0025 mole) triethylamine. Dissolution of the tellurenyl iodide and formation of a pasty brown product in the red solution was observed. The same results were obtained when larger amounts

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[18] H. Rheinboldt and E. Giesbrecht, *Chem. Ber.* **88**, 676 (1955)

of triethylamine (until 2·5 g) are employed. The benzenic solution was concentrated and treated with pet. ether (30–50°). The ditelluride separates as red needles (50–75%), m.p. 120–122°. The pasty product was extracted with benzene. From the hot benzene solution small amounts of triethylammonium iodide separated 0·080 g (14%), colourless needles, m.p. 180°. The brownish residue (0·40–0·50 g) melted above 100°, gave positive test for Te and I_2, and on treatment with NaOH aq it liberated free triethylamine. The residue could not be further purified.

Reaction of triethylamine with iodine

Treating triethylamine with iodine in several proportions, triethylammonium iodide was not formed, only paste indefinite products being obtained.

Reaction of tri-isopropyl phosphite with 2,4-dinitrophenylselenenyl bromide

A solution of 1·63 g (0·005 mole) 2,4-dinitrophenylselenenyl bromide in 20 cc benzene was treated with 1·04 g (0·005 mole) tri-isopropyl phosphite. The diselenide filtered off 1·20 g (94%), m.p. 264–265° after recrystallization in the usual manner. The filtered solution was evaporated *vacuo*, the residue dissolved in ether and treated with 1·0 g aniline. After 12 hr the aniline hydrobromide was separated by filtration. The ethereal solution was evaporated and the crystalline diisopropyl N-phenylaminophosphonate was separated from the residual oil over a porous plate, 0·45 g (70%). On recrystallization from pet. ether (50–70°), it formed colourless prism m.p. 120° (in accord. with lit.[14]).

Reaction of tri-isopropylphosphite with 2-naphthyltellurenyl iodide

A suspension of 0·95 g (0·0025 mole) 2-naphthyltellurenyl iodide in 10 cc benzene was treated with 0·52 g (0·0025 mole) tri-isopropylphosphite. To the red solution pet ether (30–50°) was added. Red needles of the ditelluride precipitated, 0·32 g (51%), m.p. 120–122°. The filtrate was treated as in the preceding experiment, giving 0·28 g (89%) of the phenylaminophosphonate.

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