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Registry No. I, 55669-46-0; II, 55669-47-1; $Na_2Fe(CO)_4$, 14878-31-0; 1,2-dichlorotetramethyldigermane, 22702-77-8.

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Dibenzotellurophene. A New Synthesis by Way of 2-Biphenylyltellurium Trichloride

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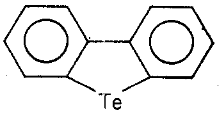
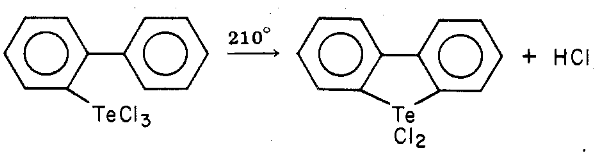
Several syntheses of dibenzotellurophene, I, have been reported. The two earliest methods[1,2] give very poor yields and the procedures require close attention for long periods. More recently, two syntheses[3] have been reported to give good yields in the final steps, but since the starting materials are not readily available, additional time and effort would be required for their preparation. The procedure which gives good yields of dibenzoselenophene[4] cannot be applied directly to the tellurium compound because the preparation of useful quantities of potassium tellurocyanate, KTeCN, in aqueous solution appears to be impossible.[5] In spite of this difficulty, a ring-closing step similar to that in the dibenzoselenophene synthesis is useful here, namely, the spontaneous conversion of 2-biphenylyltellurium trichloride, II, at ~210° to dibenzotellurophene dichloride, III, which proceeds in quantitative yield. The dichloride is reduced to dibenzotellurophene by potassium pyrosulfite, $K_2S_2O_5$.



I



(1)

II III

The previously unreported 2-biphenylyltellurium trichloride was prepared by two different methods. One of these was patterned after the procedure used by Campbell and Turner[6] for the preparation of some phenoxatellurin derivatives. While several steps are involved, each is fairly easy to carry out in reasonably good yield. As applied to the dibenzotellurophene synthesis, the steps take the form of eq 2–4 in which the symbol Ar represents the 2-biphenylyl group. The second method involves reactions 5 and 6. While the latter procedure is more

$$ArNH_2 \xrightarrow[NaNO_2]{H_2SO_4} ArN_2^+ \xrightarrow[HgCl_2]{HCl} (ArN_2)_2Hg_2Cl_6 \quad (2)$$

$$(ArN_2)_2Hg_2Cl_6 \xrightarrow[-60°]{Cu\ in\ (CH_3)_2CO} ArHgCl + N_2 + CuCl \quad (3)$$

$$ArHgCl + TeCl_4 \xrightarrow[reflux]{CHCl_3} ArTeCl_3 + HgCl_2 \quad (4)$$

$$ArBr + n\text{-BuLi} \xrightarrow[-60°]{Et_2O} ArLi + n\text{-BuBr} \quad (5)$$

$$ArLi + TeCl_4 \xrightarrow{Et_2O} ArTeCl_3 + LiCl \quad (6)$$

direct, the reaction conditions (rigorous exclusion of moisture and oxygen) are more exacting and the yields are poorer, probably due in part to the fact that some of the $ArTeCl_3$ already formed also reacts with ArLi to give Ar_2TeCl_2, etc. In fact, Wittig and Fritz[7] have used a similar reaction to prepare tetraphenyltellurium.

Preparations of dibenzotellurophene dibromide and dibenzotellurophene diiodide are also described.

Experimental Section

Physical Measurements. Melting points were measured in open capillaries and are uncorrected. All of the halogenated tellurium compounds reported here decompose appreciably before melting. In these cases the recorded melting points were taken on samples immersed in the bath about 5° below the recorded value. Microanalyses were carried out by Miss Heather King in this department. X-Ray diffraction data on two of the compounds were taken on the Syntex $P\bar{1}$ autodiffractometer.

Materials. All chemicals and solvents used were reagent grade except as noted below. 2-Aminobiphenyl (Eastman, practical grade), 2-bromobiphenyl (K and K Laboratories), and tellurium tetrachloride (Alfa Inorganics) were used without further purification. Diethyl ether was dried over sodium and distilled as needed under N_2 atmosphere. Acetone was dried over Linde Molecular Sieves, Type A, and chloroform was passed through a column of active basic aluminum oxide (EM Laboratories, Activity I) to remove water and methanol. *n*-Butyllithium (Alfa Inorganics) was in the form of a 2.2 *M* solution in hexane.

2-Biphenylylmercury Chloride. A solution of 34 g (0.20 mol) of 2-aminobiphenyl in 30 ml of warm concentrated sulfuric acid was added with stirring to 1.0 l. of ice water. A solution of 14 g (0.20 mol) of sodium nitrite in 25 ml of cold water was then slowly added to the mechanically stirred amine bisulfate solution. After about 10 min, the diazotized amine solution was added in small (5–10 ml) increments to a mechanically stirred solution of 54 g (0.20 mol) of mercury(II) chloride in 60 ml of concentrated hydrochloric acid and 50 g of ice in a 2-l. beaker. The finely divided pale yellow precipitate was filtered off and washed twice with water, then with absolute ethanol, and finally with anhydrous ether.

The diazonium salt, formulated here as $(C_{12}H_9N_2)_2Hg_2Cl_6$, was placed in a 1-l. conical flask, mixed well with 400 ml of anhydrous acetone and cooled externally with Dry Ice to ca. −60°. Copper powder was prepared by adding 26 g (0.40 mol) of zinc dust in ~0.5-g portions to a mechanically stirred solution of 125 g (0.50 mol) of $CuSO_4 \cdot 5H_2O$ in 400 ml of freshly boiled water. The filtered copper powder was washed with water and then with dry acetone and stirred into the diazonium salt–acetone mixture. The flask was loosely covered with an inverted beaker and packed in Dry Ice in a well insulated container so that the reaction mixture would remain at ca. −60° for 24–36 hr; then it was allowed slowly to warm up to room temperature. After evolution of nitrogen gas had stopped, the mixture was filtered and the residue was extracted with two 100-ml portions of hot acetone. The extracts and filtrate were combined and concentrated to approximately 200 ml and the product was allowed to crystallize out at 0°. Recrystallization from ethanol gave 27 g (0.069 mol, 35% yield) of white needles, mp 167.5°.[8]

2-Biphenylyltellurium Trichloride, II. Method I. A solution of 11.3 g (29.1 mmol) of 2-biphenylylmercury chloride and 7.84 g (29.1 mmol) of tellurium tetrachloride in 90 ml of dry (methanol-free) chloroform was refluxed for 1.25 hr. After cooling of the mixture to room temperature, the precipitated mercuric chloride (7.4 g, 27 mmol) was filtered off. The solution was concentrated to 20 ml and cooled to room temperature, and 8.5 g (22 mmol, 76% yield) of brilliant yellow crystals of 2-biphenylyltellurium trichloride separated. The product, recrystallized from dry chloroform, melted with decomposition at 157°. Anal. Calcd for $C_{12}H_9TeCl_3$: C, 37.23; H, 2.34; Cl, 27.47. Found: C, 36.80; H, 2.39; Cl, 27.28.

Method II. To 10.0 g (43.0 mmol) of 2-bromobiphenyl in 100 ml of dry diethyl ether cooled to ca. −60° under nitrogen, 20 ml of 2.2 *M* *n*-butyllithium in hexane was slowly added with efficient stirring. The solution became yellow at first; then a pale yellow finely divided solid separated. The mixture was stirred for 1 hr as it was allowed to warm to room temperature. The resulting suspension was added dropwise with stirring to a solution of 11.3 g (42.0 mmol) of tellurium tetrachloride in 150 ml of dry diethyl ether under nitrogen. A greenish-brown solid separated during the addition and the mixture was cooled externally with ice water as required to keep the reaction mixture at or below room temperature. Stirring was continued for 1 hr after which the mixture was filtered and the solid was extracted with 50 ml of hot, dry chloroform. After reduction of the volume to 15 ml and standing overnight, 2.6 g (6.7 mmol, 16% yield) of yellow crystals of 2-biphenylyltellurium trichloride (mp 157°) resulted.

Dibenzotellurophene Dichloride, III. A 2.409-g (6.222-mmol) sample of recrystallized 2-biphenylyltellurium trichloride was placed in an open test tube and heated in refluxing nitrobenzene (ca. 210°). The solid melted, and hydrogen chloride was evolved from the liquid for about 5 min, after which a grayish yellow solid residue remained. The heating was continued an additional 20 min to ensure completeness of the reaction. The yield of unrecrystallized product was 2.174 g (6.199 mmol, 99.6%). Recrystallization from ethylene bromide gave pale yellow crystals melting with decomposition at 354°.[9] Anal. Calcd for $C_{12}H_8TeCl_2$: C, 41.10; H, 2.30. Found: C, 40.88; H, 2.38.

Dibenzotellurophene, I. A 1.244-g (3.55-mmol) sample of dibenzotellurophene dichloride, 25 ml of chloroform, and a solution of 4.4 g (20 mmol) of potassium pyrosulfite in 75 ml of water were placed in a 300-ml flask equipped with a magnetic stirrer. The dichloride dissolved as the reduction proceeded and the chloroform layer acquired a deep yellow color. After 2 hr of stirring, the separated chloroform layer was dried over $MgSO_4$ powder and filtered, and the solvent was allowed to evaporate in a slow stream of dry nitrogen.[10] The dibenzotellurophene crystallized as pale yellow needles melting at 94.5°.[11] The yield was 0.821 g (2.94 mmol, 82.5%). Anal. Calcd for $C_{12}H_8Te$: C, 51.51; H, 2.88. Found: C, 51.72; H, 2.80. The crystal symmetry is that of the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell for which a = 12.620 Å, b = 16.191 Å, and c = 4.637 Å. The calculated density is 1.962 g cm^{-3}.

Dibenzotellurophene Dibromide. To a solution of 0.155 g (0.558 mmol) of dibenzotellurophene in 15 ml of carbon tetrachloride, 2.0 ml of 0.29 *M* Br_2 in carbon tetrachloride was added dropwise with stirring. The pale yellow, finely divided solid which separated weighed 0.242 g (0.550 mmol) and represented a 98.6% yield. Recrystallization from ethylene bromide gave small, brilliant yellow plates which melted with decomposition at 355°.[12] Anal. Calcd for $C_{12}H_8TeBr_2$: C, 32.78; H, 1.83. Found: C, 32.95; H, 1.84.

Dibenzotellurophene Diiodide. Method I. To a solution of 0.217 g (0.775 mmol) of dibenzotellurophene in 20 ml of carbon tetrachloride, 25 ml of 0.033 *M* I_2 in carbon tetrachloride was added dropwise with stirring. The finely divided, deep orange precipitate which separated weighed 0.405 g (0.760 mmol) and represented a 98% yield. Recrystallization from ethylene bromide gave small, brilliant, garnet red plates which melted with decomposition at 335°.[13] Anal. Calcd for $C_{12}H_8TeI_2$: C, 27.01; H, 1.51. Found: C, 27.23; H, 1.64. The crystals are triclinic with space group symmetry $P\bar{1}$. There are two molecules in the unit cell for which a = 8.807 Å, b = 8.182 Å, c = 12.001 A, α = 121.16°, β = 101.63°, and γ = 103.05°.[14] The calculated density is 2.660 g cm^{-3}.

Method II. Dibenzotellurophene dichloride (0.598 g, 1.70 mmol) and potassium iodide (1.80 g, 10.8 mmol) were ground together in a mortar under 20 ml of 2-butanone for about 5 min. The dark red-brown solution was decanted through a glass filter and the solvent was permitted to evaporate. The product consisted mainly of deep red prismatic crystals of the diiodide along with some colorless crystals of potassium chloride and/or iodide. The latter were readily leached out by several rinsings with water, leaving 0.749 g (1.40 mmol, 83% yield) of the diiodide. These crystals are considerably larger and quite different in habit when compared to those crystallized from ethylene bromide in method I. However, elemental analysis and X-ray diffraction data show that the products from the two methods are chemically identical.

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Registry No. 2-Biphenylylmercury chloride, 10271-66-6; 2-aminobiphenyl, 90-41-5; mercury(II) chloride, 7487-94-7; tellurium tetrachloride, 10026-07-0; 2-bromobiphenyl, 2052-07-5; dibenzotellurophene dibromide, 55493-63-5; dibenzotellurophene diiodide, 1818-19-5; I, 244-98-4; II, 55493-62-4; III, 1818-18-4.

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(8) The melting point of this compound has been reported in three previous communications: Courtot and Bastani[1] gave 165–167°; G. Wittig and W. Herwig, *Chem. Ber.*, **88**, 962 (1955), gave 161–162.5, 162.5–163, and 161–162° for products prepared by three different methods; G. Bähr and R. Gelins, *ibid.*, **91**, 812 (1958), gave 166–167°.

(9) The melting point of the dichloride is given as 333–335° in ref 3, but ref 1 gives a decomposition temperature of about 200°.

(10) Solutions of dibenzotellurophene become turbid when exposed to moist air, probably due to oxidation at the tellurium atom.

(11) The melting point of dibenzotellurophene is given as 91–92° in ref 1 and 93° in ref 2.

(12) The decomposition temperature of the dibromide is given as 210–220° in ref 1.

(13) The melting point of the diiodide is given as 335–340° in ref 3.

(14) A complete structural study of dibenzotellurophene diiodide has been reported: J. D. McCullough, *Inorg. Chem.*, **14**, 1142 (1975).

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Five-Coordinate Complexes of Ruthenium(II) with Di(tertiary phosphines)

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Several six-coordinate complexes of ruthenium(II) with diphosphine ligands have been reported in the last years. The major work has been done by Chatt and Hayter,[1] who prepared complexes of the general formula $[RuX_2(diphosph)_2]$ and $[RuXY(diphosph)_2]$, where X and Y are anionic ligands such as halogenides, pseudohalogenides, hydrides, or σ-bonded alkyl and aryl groups. The di(tertiary phosphines) used are generally of the type $R_2P(CH_2)_nPR_2$ (n = 1, R = C_6H_5; n = 2, R = CH_3, C_2H_5, C_6H_5). No five-coordinate complexes of the type $[RuX(diphosph)_2]^+$ appear to be isolated. However, the chemical behaviors of some of these octahedral complexes, which can react with neutral ligands to give six-coordinate cationic derivatives of the type $[RuX(L)(diphosph)_2]^+$,[1-3] indirectly suggest the possibility of formation of five-coordinate cations $[RuX(diphosph)_2]^+$. With the aim of obtaining such unsaturated species, we have begun an investigation on the complexes formed by ruthenium(II) with a series of bidentate ligands.

We report here the first results, obtained with the di-