A NEW APPROACH TO THE SYNTHESIS OF TELLURANTHENE

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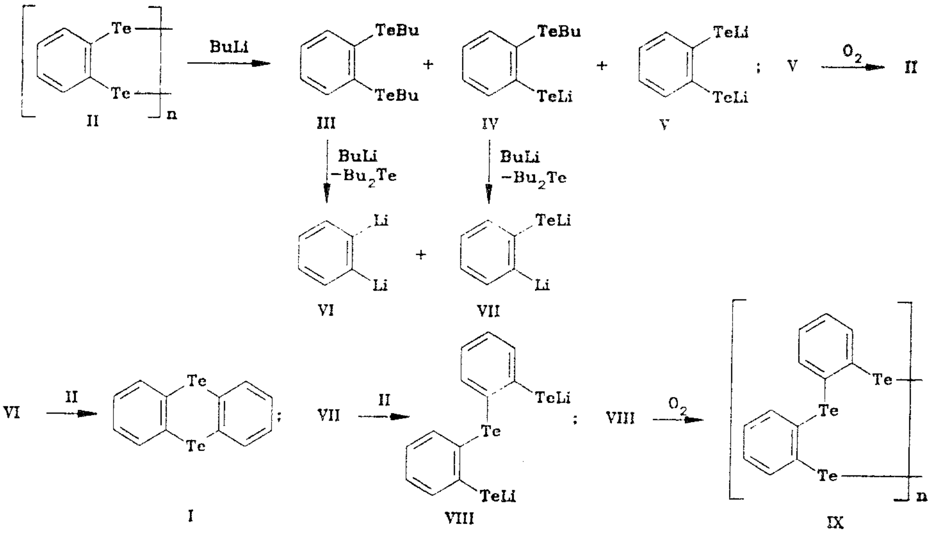
UDC 547.818.9:542.941:
543.422.72

A series of new methods of synthesizing telluranthrene are proposed, based on the use of poly(o-phenylene)ditelluride and its precursors. The best yields of telluranthene are obtained by the reactions of the disodium salt of o-ditellurolobenzene with o-diiodobenzene (50-62%) and of poly(o-phenylene)ditelluride with butyllithium.

The only synthesis of telluranthrene (I) described prior to our paper [1] is based on the reaction of the rather difficultly obtainable hexameric o-phenylenemercury with powdered tellurium at 250°C and gives compound I in 70% yield [2]. A report of the synthesis of compound I by heating tetraphenyltin with elementary Te [3] was not confirmed [2]. We have proposed new methods of preparing telluranthrene from poly(o-phenylene)ditelluride (II) [4], which we recently synthesized, and some of its precursors (see [1] for the previous report).

The use of poly(o-phenylene)ditelluride, II, for preparing telluranthene is based on known reactions in the chemistry of organic tellurium compounds: 1) the breaking of the Te—Te bond in diarylditellurides under the action of organic magnesium [5] and lithium [5] compounds to form aryl(organyl)tellurides and tellurophenolates, ArTeMgX or ArTeLi; 2) the rupture of a C—Te bond in diorganyltellurides in the reaction of the latter with lithiumalkyls, leading to alkyl(organyl)tellurides and organolithium derivatives [6].

The treatment of polyditelluride II with a fourfold excess of butyllithium in ether solution leads to the formation of telluranthrene I in 26% yield. A probable mechanism of this synthesis, taking account of the data in [5, 6] is shown below.



The reaction of polytelluride II with butyllithium probably leads to the formation of compounds III-V. The dilithium derivative of o-tellurobenzene, V, changes to polytelluride II during the subsequent treatment of the reaction mixture. Di(o-butyltelluro)benzene (III) is apparently transformed into o-dilithiumbenzene (VI) and the dilithium derivative, VII, on further reaction with butyllithium. Compound VII is obtained by the reaction of intermediate IV with butyllithium together with dibutyltelluride. The reaction of compound VI with polytelluride II leads to the

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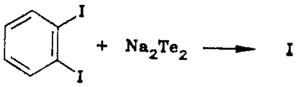
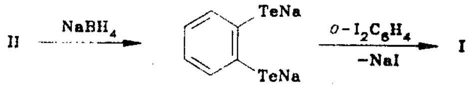
formation of compound I. Moreover, on reaction with polytelluride II, derivative VII is converted to compound VIII, which is transformed into a mixture of poly(o-phenylene)telluride (ditelluride) IX by the action of water and atmospheric oxygen. Telluranthrene is easily separated from the reaction mixture thanks to its enormous solubility compared to that of polymers II and IX. The latter are virtually insoluble in any of the ordinary organic solvents; hence their formation could not be confirmed experimentally, but is based only on the usual reactions of organotellurium compounds presented above [5, 6].

The preparation of telluranthene in 12% yield in the reaction of o-diiodobenzene with Na_2Te_2, synthesized from the elements in hexamethylphosphotriamide (HMPTA) was unexpected. Actually, o-haloarenes give diarylditellurides on reaction with Na_2Te_2 in polar, aprotic solvents (DMF, HMPTA, N-methyl-pyrrolidone) [7], though in low yield. When o-dibromobenzene is treated with Na_2Se_2 in DMF, it is converted into (o-phenylene)diselenide in 26% yield [8].

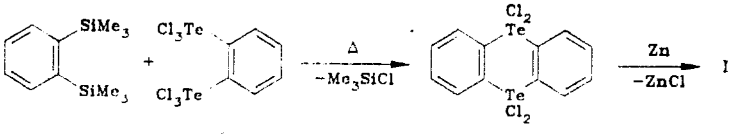


From the preparative point of view, the most convenient method of synthesizing telluranthrene is the reaction of the disodium derivative of o-ditellurobenzene (X) with o-diiodobenzene [1]. Readily generated in situ by the reduction of polytelluride II with sodium borohydride in DMF, the disodium derivative, X, reacts with o-diiodobenzene to give compound I in a 50-62% yield.



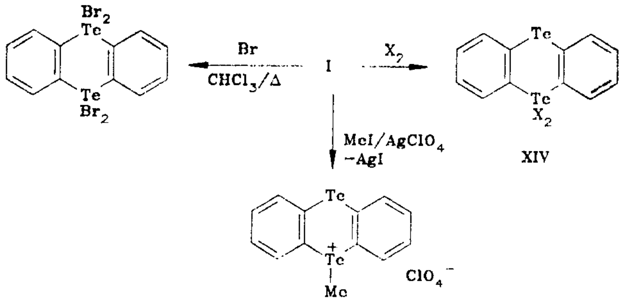
X

Yet another of the approaches to the synthesis of telluranthrene, I, that we have proposed is based on the use of bis(o-trimethylsilyl)benzene (XI) as a starting material [4]. Just as aryltrimethylsilanes reacting with aryltellurotrichlorides give moderate yields of diaryltellurodichlorides [9], compound XI reacts with bis(o-trichlorotelluro)benzene (XII) [4], leading to the formation of 5,5,10,10-tetrachlorotelluranthene (XIII). When, with no further purification, the latter is reduced with zinc dust in isopropanol, telluranthrene I is obtained in 16% yield.



XI XII XIII

We have studied some of the reactions of telluranthene, concerning which information is lacking in the literature. Like other tellurium derivatives [10, 11], including heterocyclic ions [12, 13], telluranthrene readily changes into derivatives of tetra- and tricoordinated tellurium. The composition of the tetracoordinated derivatives depends on the temperature at which the reaction is carried out. Thus, in the reaction with Cl_2 or Br_2 at 0-5°C, the dihalotelluranthrene, XIV, is formed, whereas the reaction of heterocycle I with excess bromine in boiling $CHCl_3$ leads to the formation of tetrabromotelluranthrene (XV). As with other tellurium-containing heterocycles [12, 13], telluranthrene is converted to methyltelluranthrenium perchlorate (XVI) when treated with methyl iodide in the presence of an equimolar amount of $AgClO_4$.



XIV

XVI

XIV a X=Br; b X=Cl

EXPERIMENTAL

Bis(o-trichlorotelluro)benzene (XII) and poly(o-phenylene)ditelluride II were synthesized according to [4].

Reaction of Poly(o-phenylene)ditelluride with Butyllithium. Over a 30-min period, add 62 ml of 2.35 N butyllithium in hexane with stirring under an argon atmosphere to a suspension of 12.0 g (36.4 mmoles) of compound II in 120 ml of absolute ether placed in a three-necked flask equipped with a stirrer, a dropping funnel, and a tube for the introduction of argon and refluxing. The color of the solution changes from red to pink. Boil the mixture with stirring for 2 h, pour it onto 200 g of finely ground ice, filter off the deposit that forms (4.2 g), separate the organic layer, and extract the aqueous layer with ether (3 × 50 ml). Combine the ethereal extracts, wash, dry over $CaCl_2$, and evaporate off the solvent. Dissolve the residue in 50 ml of CCl_4 and treat with excess bromine while stirring and cooling at 0-5°C (the reaction mixture turns red). Filter off the precipitate of dibromotelluranthrene, XIVa, that forms, wash with ether and dry. Yellow needles with $T_{mp} > 360°C$ (from a DMSO/$CHCl_3$ mixture). Yield 2.7 g (26%).

Following [10], treat the dibromotelluranthrene with an aqueous solution of $Na_2S_2O_5$ to obtain a practically quantitative yield of telluranthrene, I, in the form of yellow prisms with T_{mp} 167-168°C (from hexane); according to [2], T_{mp} is 169-170°C.

Treat the oily residue that forms when the solvent is evaporated from the filtrate after the separation of dibromotelluranthrene with an aqueous solution of $Na_2S_2O_5$ by the method in [10] to obtain dibutyltelluride in the form of a light yellow liquid with T_{bp} 108-110°C (11 mm Hg); according to [11], T_{bp} is 109-112°C (12 mm Hg). Yield 3.9 g.

Telluranthrene (I). A. Pour dropwise with stirring under an argon atmosphere a solution of 1.51 g (40 mmoles) of $NaBH_4$ in 20 ml of DMF to a suspension of 3.31 g of compound II (10 mmoles calculated as the monomeric unit) in 50 ml of absolute DMF placed in a three-necked flask equipped as in the first synthesis. The mixture spontaneously heats up to 100°C, and the solution becomes bright red in color. Cool the solution of the disodium derivative of o-ditellurolobenzene to 20°C, add a solution of 3.3 g (10 mmoles) of o-diiodobenzene in 10 ml of DMF, and heat at 100°C for 1 h. After cooling the reaction mixture, pour it into 200 ml of water, extract with $CHCl_3$ (3 × 50 ml), combine the organic layers, wash with water (2 × 50 ml), dry over $CaCl_2$, and treat with bromine as described above. Yield of compound XIVa 3.52 g (62%). After reduction with $Na_2S_2O_5$, compound I is obtained in practically quantitative yield.

B. Add 2.3 g (100 mmoles) of sodium in small portions with vigorous stirring to a suspension of 12.7 (100 mmoles) of powdered tellurium in 100 ml of freshly distilled HMPTA at 90°C in a stream of argon. Stir for 2 h at 90°C to form a dark violet solution of Na_2Te_2, cool to 5°C, and add to it dropwise with stirring 10.5 g (50 mmoles) of o-diiodobenzene. Stir for 2 h at 110°C, then for 10 h at 150°C. After cooling the reaction mixture, pour it into 200 ml of water, filter off the tellurium residue (8.7 g), and extract the filtrate with $CHCl_3$ (4 × 30 ml). Treat the chloroform extract as described above to obtain 1.22 g (12%) of telluranthrene.

C. Stir a mixture of 5.44 g (10 mmoles) of bis(o-trichlorotelluro)benzene and 10 ml of bis(o-trimethylsilyl)benzene at 210-220°C for 30 min. Cool the reaction mass, filter off the deposit of compound XIII, wash with $CHCl_3$, and dry. Reduce substance XIII with zinc dust in isopropanol as described in [10] to obtain 0.66 g (16%) of telluranthene.

Dibromotelluranthrene (XIVa, $C_{12}H_8Br_2Te_2$). Add a solution of 0.5 g (3.1 mmoles) of bromine in 10 ml of CCl_4 dropwise with stirring to a solution of 1 g (2.4 mmoles) of telluranthrene, I, in 20 ml of CCl_4 cooled to 0-5°C in an ice bath. Filter off the yellow precipitate that forms, wash with CCl_4, and dry. Fine, yellow prisms with $T_{mp} > 360°C$ (from a DMSO/$CHCl_3$ mixture). Yield 1.36 g (100%).

Dichlorotelluranthrene (XIVb, $C_{12}H_8Cl_2Te_2$). Pass a current of dry chlorine through a solution of 1 g (2.4 mmoles) of compound I in 30 ml of $CHCl_3$ for 20 min at 0-5°C. Filter off the colorless precipitate that forms, wash with $CHCl_3$, and dry. Fine, colorless prisms with $T_{mp} > 360°C$ (from a DMSO/$CHCl_3$ mixture). Yield 1.14 g (100%).

Tetrabromotelluranthrene (XV, $C_{12}H_8Br_4Te_2$). Reflux a solution of 1 g (2.4 mmoles) of telluranthrene, I, and 1.2 g (7.5 mmoles) of bromine in 20 ml of $CHCl_3$ for 20 min. Filter off the light yellow precipitate that forms after the mixture is cooled, wash with $CHCl_3$, and dry. Almost colorless prisms with $T_{mp} > 360°C$ from a DMSO/$CHCl_3$ mixture. Yield 1.74 g (100%).

Methyl Telluranthrenium Perchlorate (XVI, $C_{12}H_{11}ClO_4Te_2$). Add a solution of 0.16 g (1.1 mmoles) of CH_3I in 2 ml of acetone to a solution of 0.41 g (1 mmole) of compound I in 20 ml of acetone and immediately add, with stirring, a solution of 0.33 g (1 mmole) of $AgClO_4 \cdot 3CH_3CN$ in 10 ml of acetone. Boil the solution for

5 min, cool, filter off the precipitate of AgI, and evaporate the filtrate to half the volume. Filter off the light gray crystals that precipitate and wash with ether. T_{mp} 326-328°C (with detonation). Yield 0.37 g (71%).

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