

## Tellurium Tetrachloride

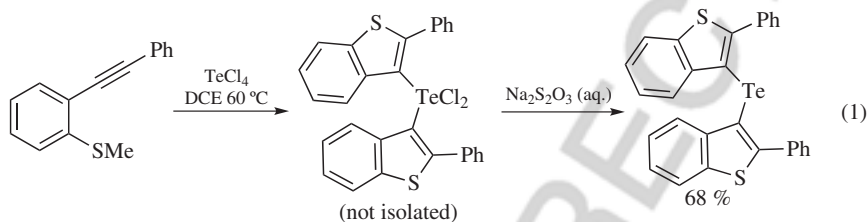
Q1

[10026-07-0]  $\text{TeCl}_4$  (MW: 269.41)  
 InChI = 1S/Cl4Te/c1-5(2,3)4  
 InChIKey = SWLJJEFPJUCUBD-UHFFFAOYSA-N

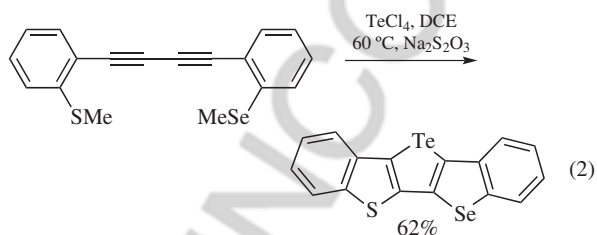
Physical Data: mp 224 °C, bp 380 °C, density 3.26 g mL<sup>-1</sup> at 25 °C.

Form Supplied in: powder, crystals, or chunks.

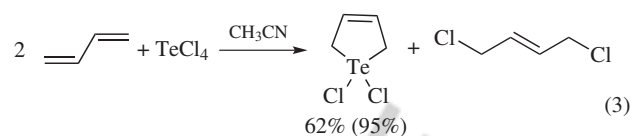
**Cyclization Reactions.**  $\text{TeCl}_4$  acts as a bis-electrophile in the reaction with a simple alkyne. It performed well in the double-electrophilic cyclization (DEC) of methyl 2-(phenylethynyl)phenyl sulfide when reacted in 1,2-dichloroethane (DCE) at 60 °C to give the dibenzo[b]-thiophenyl telluride. In the reaction with  $\text{TeCl}_4$ , the initial product formed was the dibenzo[b]thiophenyl dichlorotelluride, which converted to telluride upon reductive workup ( $\text{Na}_2\text{S}_2\text{O}_3$ ) (eq 1).<sup>1</sup>



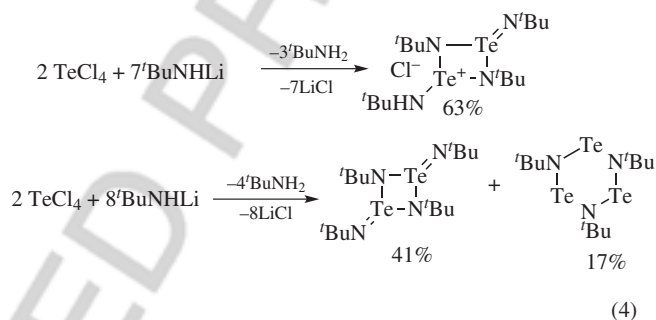
DEC of the mixed selenosulfide with  $\text{TeCl}_4$  followed by reductive workup ( $\text{Na}_2\text{S}_2\text{O}_3$ ) produced the first reported heteroacene containing all three thiophene, selenophene, and tellurophene heterocycles (62%) (eq 2).<sup>1</sup>



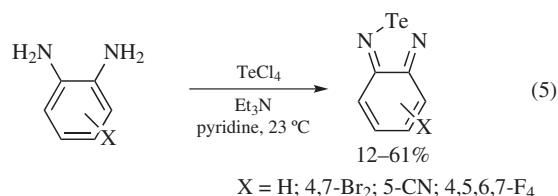
It was found that  $\text{TeCl}_4$  adds reproducibly to butadiene in refluxing acetonitrile forming 2,5-dihydrotellurophene 1,1-dichloride (62% yield) and 1,4-dichloro-2-butene. When the reaction was carried out in toluene, the yield could be improved to 95%, but unfortunately the reaction was not reproducible in this solvent, often depositing large amounts of elemental tellurium (eq 3).<sup>2</sup>



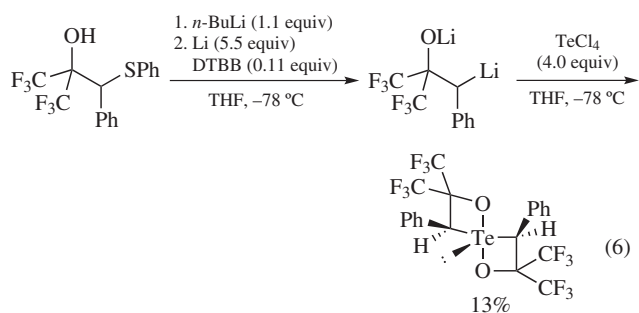
The reaction of  $\text{TeCl}_4$  with  $t\text{BuNHLi}$  in toluene at  $-100\text{ }^\circ\text{C}$  (followed by slow warming to  $23\text{ }^\circ\text{C}$ ) gives rise to three products, in amounts that depend on the molar ratio of the reactants. When the ratio was 2:7, the major product was isolated in 63% yield as very moisture-sensitive yellow crystals. When the molar ratio of  $\text{TeCl}_4$  to  $t\text{BuNHLi}$  was 1:4, the two products were isolated in 41 and 17% yield, respectively (eq 4).<sup>3</sup>



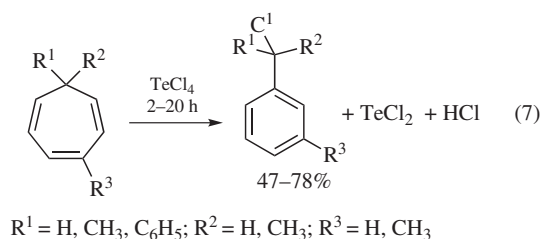
Moisture-sensitive benzochalcogenadiazoles were synthesized from 1,2-phenylenediamines by the action of  $\text{TeCl}_4$  in pyridine at  $23\text{ }^\circ\text{C}$  (eq 5).<sup>4</sup>



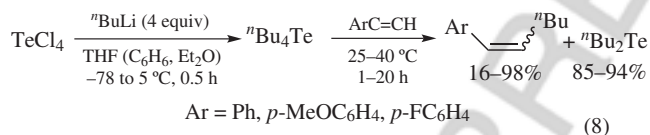
The direct substitution of tellurium tetrachloride with  $\text{LiCHPhC}(\text{CF}_3)_2\text{OLi}$  generated by Yus' method involves successive treatment of hydroxyalkyl phenyl sulfide with  $n\text{-BuLi}$  and excess metallic lithium in the presence of a catalytic amount of 4,4-di-*t*-butylbiphenyl (DTBB) in THF at  $-78\text{ }^\circ\text{C}$ . Adding excess of  $\text{TeCl}_4$  at  $-78\text{ }^\circ\text{C}$  and further warming to the room temperature gave a single isomer of 1,5-dioxo-4,4-telluraspiro[3.3]heptane in 13% yield as an air stable solid (eq 6).<sup>5</sup>



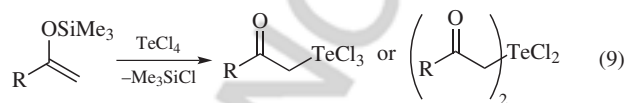
**Addition Reactions.** The use of tellurium tetrachloride as a reagent was studied for different substrates and proceeded at low temperature (0–5 °C) in good yield (eq 7).<sup>6</sup>



Tetrabutyltellurium was prepared by the reaction of  $\text{TeCl}_4$  with 4 equiv of  $n\text{-BuLi}$  in diethyl ether at 0 °C and with 1 equiv of aryl acetylenes at room temperature to afford butyl addition products (eq 8).<sup>7</sup>

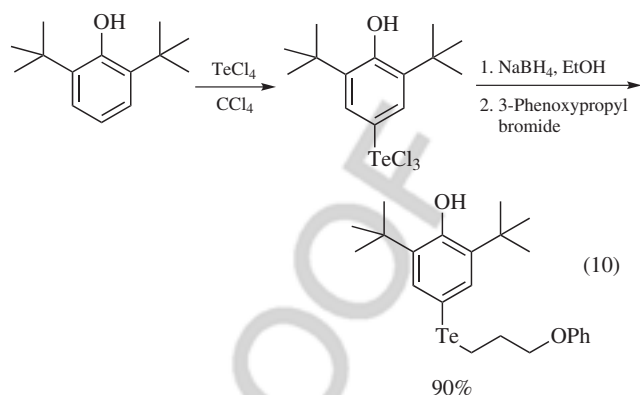


The reaction with silyl enolethers was found to proceed under mild conditions to give two products, the ratio depending on the amount of  $\text{TeCl}_4$ . The equilibrium between products was also examined (eq 9).<sup>8</sup>

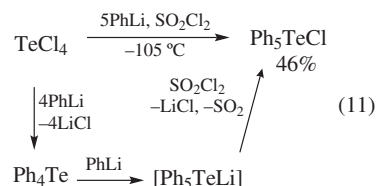


$R = \text{Me, } n\text{-heptyl, } i\text{-Bu, } t\text{-Bu, } 1\text{-adamantyl, Ph, } p\text{-MeOC}_6\text{H}_4$

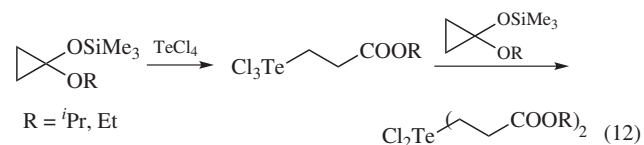
3,5-Di-*tert*-butyl-4-hydroxyphenyl 3-phenoxypropyl telluride was obtained in 90% overall yield from commercially available 2,6-di-*tert*-butylphenol by reaction with tellurium tetrachloride followed by sodium borohydride reduction of the resulting aryltellurium trichloride to a tellurolate and alkylation with 3-phenoxypropyl bromide (eq 10).<sup>9</sup>



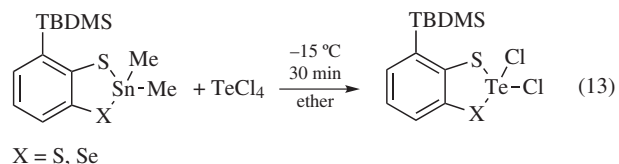
$\text{Ph}_5\text{TeLi}$  was prepared by reaction of 5 M equiv of  $\text{PhLi}$  with 1 equiv of  $\text{TeCl}_4$  in THF at –105 °C. Treatment of this material  $\text{Ph}_5\text{TeCl}$  with  $\text{SO}_2\text{Cl}_2$  provided  $\text{Ph}_5\text{TeCl}$ . Since the one-pot reaction involves the intermediate generation of  $\text{Ph}_4\text{Te}$ , the temperature was maintained at –78 °C for 2 h after the addition of 4 M equiv of  $\text{PhLi}$  to  $\text{TeCl}_4$ . The reaction mixture was concentrated in vacuo, and the residue was washed with acetonitrile and recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexane (eq 11).<sup>10</sup>



Tellurium tetrachloride readily reacted with cyclopropanone ketals in a stepwise manner, giving the monoalkyltellurium compound and the dialkyl compound in accordance with the stoichiometry of the reagents (eq 12).<sup>11</sup>

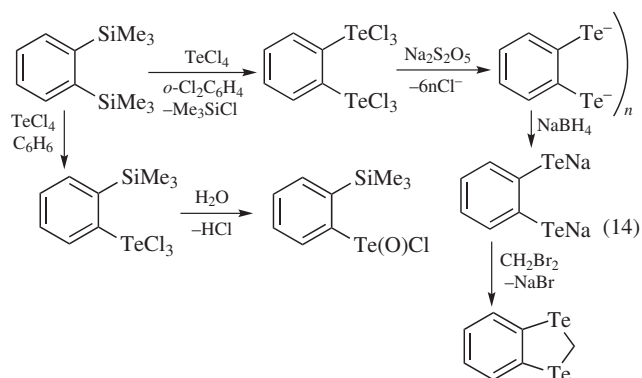


**Substitution Reactions.** 4-*tert*-Butyldimethylsilyl-2,2-dimethylbenzo[1,2-d][1,3,2]dichalcogenastannoles, synthetic equivalent of unstable ortho benzeneditelluraols, were prepared by the ortho lithiation followed by stannylation (eq 13).<sup>12</sup>

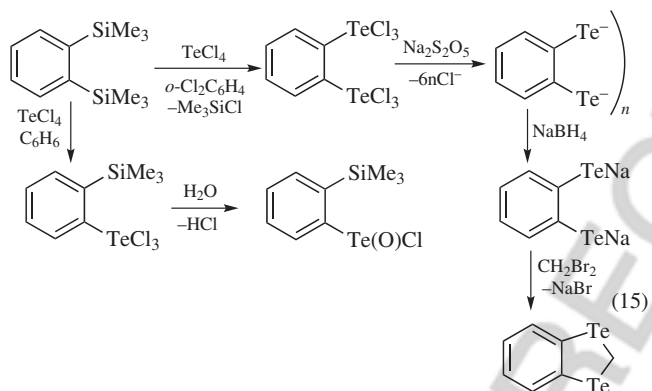


A tellurane was synthesized by two methods in excellent yields. 4,7-Diisopropyl-2,2-dimethyl-1,3,2-benzodithiastannole was reacted with an equimolar amount of 2,2-dichloro-4,7-diisopropyl-1,3,2-benzodithiatellurolate at –78 °C under argon to give the desired tellurane, 2,2-spirobi[4,7-diisopropyl-1,3,2-benzodithiatellurolate] in 100% yield. Alternatively, 4,7-diisopropyl-2,2-dimethyl-1,3,2-benzodithiastannole reacted with

a half-molar amount of tellurium tetrachloride at  $-78^{\circ}\text{C}$  under an argon atmosphere to give the tellurane in 82% yield (eq 14).<sup>13</sup>



Benzo-1,3-ditellurole was prepared by a four-step synthetic procedure starting from 1,2-bis(trimethylsilyl)benzene. The substitution of both trimethylsilyl groups by  $\text{TeCl}_3$  groups occurs via heating in  $o$ -dichlorobenzene at reflux for 2 h to afford 1,2-bis(trichlorotelluro)benzene in 46% yield. Using solvents with lower boiling points (benzene or toluene), only allows substitution of one trimethylsilyl group, giving rise to  $o$ -trimethylsilyl(trichlorotelluro)benzene (eq 15).<sup>14</sup>



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### Author Query

- Q1** Please provide the structure of the title compound.
- Q2** Please provide the key for the title compound.
- Q3** Please check if the intended meaning of the sentence “Tetrabutyltellurium was...butyl addition products.” is retained after the edits.

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