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Tellurium tetrachloride: an improved method of preparation

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Abstract

An efficient and practical synthesis of tellurium tetrachloride from elemental tellurium and sulfuryl chloride is described.

Keywords: Tellurium tetrachloride; Sulfuryl chloride; Tellurium

Tellurium, once regarded as an exotic chemical element, became the key component of a variety of versatile and useful reagents for organic synthesis. The multiple applications of organotellurium chemistry have been well described in a number of review articles and books.[1–8]

Of the many inorganic tellurium reagents employed to introduce tellurium in organic substrates, such as elemental tellurium, alkali tellurides and ditellurides, hydrogen telluride and tellurium dioxide, tellurium tetrachloride deserves a special role. $TeCl_4$ reacts with activated aromatic compounds, with organo-chloromercury compounds, with aromatic Grignard reagents and with several active methylene groups; adds to double and triple C–C bond; and participates in the synthesis of tellurium heterocycles.[8]

Tellurium tetrachloride has been usually prepared by the reaction of elemental tellurium with chlorine gas. In spite of the high yields attained, the procedure is rather tedious and laborious, certainly in agreement with the opinion of previous researchers, since a particular glass apparatus[8,9] is used, in which the tellurium tetrachloride produced is distilled under a continuous chlorine stream into connected tubes. After solidification of the product, the tubes are detached from the apparatus. By this procedure, tellurium tetrachloride is a pale yellow crystalline solid (mp 225 °C).

We describe here a very simple and straightforword procedure for the preparation of tellurium tetrachloride, which employs sulfuryl chloride (SO_2Cl_2) as chlorine source (Scheme 1).

By heating at reflux a suspension of elemental tellurium in excess of sulfuryl chloride, a white to light-gray solid of the tellurium tetrachloride is formed gradually.[10] The yield is almost quantitative. The excess of sulfuryl chloride can be recovered and reused. For most purposes, after the removal of the excess of sulfuryl chloride the reagent is ready to be used in situ. With the aim of proving the merit of this new method, some previously described reactions were performed, attaining good, compatible results:

- Reaction of $TeCl_4$ with activated aromatic compounds giving aryl tellurium trichlorides **2a**–**b** and ditellurides **3a**–**b** by $NaBH_4$ reduction in situ (Scheme 2).[11–13]
- Addition of $TeCl_4$ to phenyl acetylene giving 2-chloro-2-phenylvinyltellurium trichloride **5**, and by the use of phenyl acetylene in excess the corresponding bis-vinylic telluride **6** is formed (Scheme 3).[14,15]
- Reaction of $TeCl_4$ with 4 equiv of aryl magnesium bromides, giving symmetrical diaryl tellurides (Scheme 4).[16,17]

$$SO_2Cl_2 + Te^o \xrightarrow[\text{reflux, 12 h}]{} TeCl_4$$

Scheme 1.

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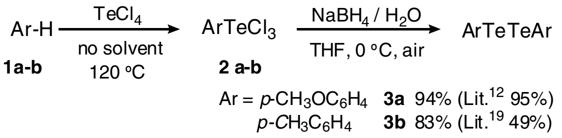
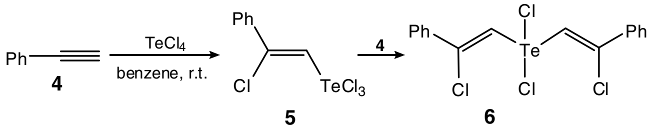
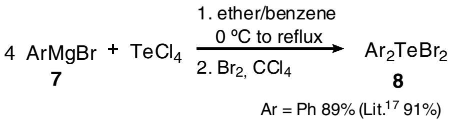


Scheme 2.

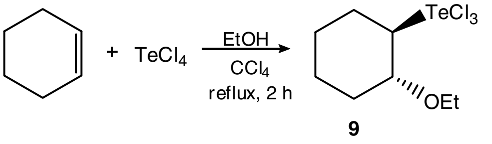


mp 205 - 210 °C; 84% (Lit.[14] 205 - 215 °C; 83%)

Scheme 3.



Scheme 4.



mp 98 - 100 °C; 66% (Lit.[18] 97 -98 °C; 63%)

Scheme 5.

– Reaction of $TeCl_4$ with alkenes, such as cyclohexene, in ethanol giving 2-ethoxy cyclohexyltellurium trichloride (**9**) (Scheme 5).[18]

By our method, the preparation of $TeCl_4$ can be performed both in small amounts (1–2 mmol) and in large amounts, such as starting with 10 g of tellurium, with comparable high yields.

In conclusion, we described here a very easy and convenient method for the preparation of $TeCl_4$ that can be used in situ for further transformations or isolated and stored. The procedure is quite simple, for example, allowing the one-pot preparation of diaryl ditellurides from elemental tellurium in very high yields.

Acknowledgement

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10. *Preparation of $TeCl_4$*: In a two neck flask, equipped with a reflux condenser and a drying tube, tellurium (10.16 g, 80 mmol) was treated with sulfuryl chloride (50 mL; excess) added dropwise. The suspension was refluxed for 12 h, cooled to room temperature and the excess of sulfuryl chloride distilled to dryness, leaving a white to light-gray solid in the flask. Argon atmosphere was then introduced. The solid was washed with dry hexanes (2 × 50 mL), the solvent removed with a syringe and $TeCl_4$ is ready to use for most purposes. It can be further dried under vacuo and transferred to a glass bottle. Isolated yield: 19.71 g (91.6%); mp 215 °C (lit.[9] 225 °C).
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13. *Preparation of aryltellurium trichlorides and diaryl ditellurides*: A one-necked round-bottomed flask containing tellurium tetrachloride (1.35 g, 5 mmol; prepared as above from 5 mmol of Te) was heated to 120 °C and the corresponding aromatic compound (5 mmol) was added at once, dissolving $TeCl_4$ promptly. An evolution of HCl was observed and a yellow solid was formed. The system was cooled to room temperature and the trichloride was used crude in the reduction procedure with $NaBH_4$, according to a procedure described by Comasseto.[16] *Bis(4-methoxyphenyl)ditelluride* (**3a**): Yield 1.10 g (94%); mp 57.6–59.0 °C (lit.[20] mp 58–59 °C) *Bis(4-methylphenyl)ditelluride* (**3b**): Yield 0.89 g (83%); mp 50.1–51.2 °C (lit.[19] mp 51 °C).
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