

Reductive Dialkynylation of Tellurium Tetrachloride with Lithium Amides and Terminal Alkynes

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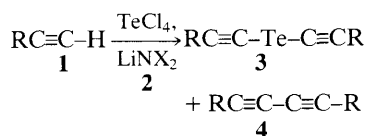
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The reaction of TeCl_4 with lithium amides such as lithium diisopropylamide and *N,N*-bis(trimethylsilyl)amide followed by treatment with terminal alkynes gives dialkynyl tellurides in moderate to high yields.

Organotellurium compounds have provided fruitful chemistry in organic synthesis over the last two decades.¹ General methods for constructing tellurium–carbon bonds utilize Te metal or TeCl_4 as an inorganic tellurium source, with valences of 0 and +4, respectively. A Te^{2-} species is also available by reducing Te powder with alkali metals and sodium borohydride. However, the lack of Te^{2+} species such as TeCl_2 because of facile disproportionation to give Te and TeCl_4 has limited preparative methods for new classes of organotellurium compounds. We have now found that the reaction of TeCl_4 –lithium amide systems, where Te^{2+} species may be

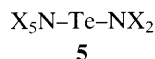
generated, with terminal alkynes affords symmetrically substituted dialkynyl tellurides (Scheme 1).

To lithium diisopropylamide (8 mmol) in tetrahydrofuran (THF) was added a THF solution of TeCl_4 (0.28 g, 2 mmol) at -78°C and the mixture stirred for 2 h at that temperature. Into the resulting orange solution was injected phenylethyne, and the mixture was stirred at -78°C for 2 h and the temperature allowed to rise to 0 – 18°C for an additional 16 h. The mixture was poured onto saturated aqueous sodium chloride, and the organic layer was extracted with Et_2O and dried over Na_2SO_4 . Purification of the crude product by silica



2a; X = Pri; 2b; X = Me₃Si

a; R = Ph
b; R = 4-MeC₆H₄
c; R = 4-MeOC₆H₄
d; R = Buⁿ
e; R = Cl[CH₂]₃
f; R = Me₃Si
g; R = HC≡C[CH₂]₄
h; R = cyclohex-1-enyl



a; X = Pri
b; X = Me₃Si

Scheme 1

gel column chromatography using n-hexane-CH₂Cl₂ as eluent gave bis(phenylethynyl) telluride **3a** and 1,4-diphenylbutadiyne **4a** in 40 and 4% yields, respectively.

The results of reactions with a variety of terminal alkynes are listed in Table 1.† Lithium *N,N*-bis(trimethylsilyl)amide **2b** was also used instead of **2a** as a base since it gave the desired dialkynyl tellurides in better yields, although a higher temperature was needed, and in some cases the butadiyne **4** was obtained as a by-product in *ca.* 20% yield. Similar treatment of SeCl₄ with **1** and **2** gave only intractable dark red solids. It is noteworthy that the reaction is applicable to both aromatic and aliphatic terminal alkynes. This is the first example of the synthesis of the aliphatic derivatives **1d–1h**.³ Furthermore, functional groups such as methoxy, chloro, silyl and alkenyl did not affect the reaction course and remained intact in the products. In the reaction of **1g**, the product **3g**, in which only one terminal alkynyl group had reacted, was obtained as a detectable product, although in moderate yield.

The present reaction may proceed *via* the tellurium diamide **5** which would be generated by the successive reduction and amination of TeCl₄ with **2** and would act as both a base and a tellurium source, since the products formed by the addition of TeCl₄ to **1** were not observed,⁴ and the reaction with two equivalents of **2** gave only a trace amount of **1**. When the temperature of the orange reaction mixture of TeCl₄ and **2a**, the mass spectrum of which showed the parent peak at 332 corresponding to **5a**, was increased to 0 °C before addition of

Table 1 Reductive dialkynylation of TeCl₄ with alkynes and lithium *N,N*-bis(trimethylsilyl)amide^a

	<i>T</i> /°C ^b	<i>t</i> /h ^b	Yield (%) of 3
1a	67	17	38
1b	0–15	16	61
1c	0–15	16	59
1d ^c	80	5	76
1e	25	16	54
1f	25	4	53
1g	67	12	24
1h	18	18	35

^a To a THF solution of a mixture of TeCl₄ (2 mmol) and LiN(SiMe₃)₂ (8 mmol) was added the terminal alkyne (4 mmol) unless otherwise noted. ^b Temperature and time after adding **1**. ^c Benzene as solvent.

1, elemental tellurium was gradually deposited as a black precipitate. Furthermore, in the reaction of **2b**, the formation of **5b** was spectroscopically confirmed in the reaction mixture in the absence of **1**.^{5,6} Recently, Björgvinsson *et al.* also isolated **2b** in *ca.* 50% yield by a similar reaction in toluene.⁷

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† The more direct route to **3**, *i.e.*, the reaction of alkynyllithium with TeCl₄ gave **3** in *ca.* 15% together with unidentified products.