Notiz / Note

A Convenient One-Pot Preparation of Bis(nitroaryl) Tellurides Using a Tellurium-Copper Couple as the Telluration Reagent

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The Te-Cu couple generated in situ by the reaction of disodium telluride with copper(I) iodide in dry *N*-methyl-2-pyrrolidone has been found to be a convenient telluration reagent for some activated iodoarenes **1**. Using this reagent system, we have prepared by a one-pot synthesis in satisfactory yields several bis(nitroaryl) tellurides **4**, which are otherwise laborious to obtain.

Elemental tellurium is generally inert toward organic compounds. Rather, the organotellurium compounds themselves tend to decompose with liberation of elemental tellurium at elevated temperatures or upon irradiation[1]. This is in marked contrast to the behavior of the lighter chalcogen elements sulfur and selenium, which undergo reactions with a variety of organic substrates under ordinary conditions[2]. However, we report in this paper that elemental tellurium, when appropriately coupled with copper, can behave as a convenient telluration reagent for some activated aromatic systems. The Te-Cu couple was obtained in situ as a black precipitate by treatment of disodium telluride (Na_2Te) with 2 equiv. of copper(I) iodide in dry *N*-methyl-2-pyrrolidone (NMP) in an inert atmosphere. This reagent reacts smoothly with iodonitroarenes **1** in NMP at 100–150°C to give the corresponding bis(nitroaryl) tellurides **4** in moderate to good yields (Table 1).

Many methods have been described for the synthesis of aromatic tellurides[1]. However, the number of nitro-containing tellurides is only limited in the literature, probably because of the sensitivity of the nitro group to arylation (Grignard and organolithium reagents) and telluration reagents (alkali tellurides and aryl tellurolates)[3] commonly employed for the synthesis of aromatic tellurides. Known procedures for the synthesis of the nitro-containing aromatic tellurides involve the reaction of aryldiazonium tetrafluoroborates with potassium tellurocyanide[4], reaction of aryl halides with aryl tellurolates[5,6], extrusion of tellurium from diaryl ditellurides by activated copper[7], oxidation of arylhydrazine with tellurium dioxide/lithium chloride to diaryltellurium dichloride followed by reductive dehalogenation with sodium pyrosulfite[8], and ligand exchange of benzyl 2-nitrophenyl telluride with 2-nitrophenyllithium[9]. However, these methods are not free from some drawbacks such as low yield, inconvenient access to starting material, use of toxic or evil-smelling reagents, tedious workup, and competing side reaction.

Results and Discussion

Disodium telluride was obtained as a purple homogeneous solution by heating tellurium and sodium hydride in NMP at 100–110°C[10]. Addition of 2 equiv. of copper(I) iodide to this solution immediately gave the Te-Cu reagent as a black suspension. The reaction of disodium telluride with copper(I) and -(II) salts has been known to form copper tellurides Cu_2Te and CuTe, respectively[11]. Several additional copper tellurides of higher order composition are also described in the literature, some of which show nonstoichiometry and occur as a component of copper ores or semiconducting materials. In view of the difference in the oxidation-reduction potentials between the telluride anion (−0.74 V) and copper(I) cation (+0.52 V)[12] as well as of the existence of free tellurium in the black precipitate, the present Te-Cu reagent might be best described as an intimate mixture of free tellurium, metallic copper and possibly some copper telluride species of unidentified composition.

An iodonitroarene (**1**) was added in one portion to the above prepared black suspension of the Te-Cu reagent, keeping an ArI-to-Te ratio of 1, and the resulting mixture was stirred at an appropriate temperature range between 100 and 150°C for 1–7 hours (Table 1). The telluration occurred smoothly, and after usual workup chromatographic purification of the crude product over silica gel gave the expected diaryl telluride **4** in a good yield. Bromonitroarenes were much less reactive and chloronitroarenes were recovered mostly unchanged under the conditions employed. With the exception of one case where 5,5'-dichloro-2,2'-dinitrobiphenyl (**5f**) was isolated in 23% yield in addition to the expected telluride **4f** in 48% yield, the Ullmann-type formation of biphenyl derivatives **5** was negligible[13]. By similar treatment, nonactivated 1-iodonaphthalene (**1i**) gave bis(1-naphthyl) telluride (**4i**) in an acceptable yield (Table 1).

NMP is the solvent of choice, and the reaction in other dipolar aprotic solvent systems always gave less satisfactory results. When commercial tellurium was finely ground and mixed intimately with commerically purchased copper powder in a 1:2 atomic ratio to replace the above prepared Te-Cu reagent, the yield of telluride **4** was very low (<3%) or almost nil. The reaction carried out under the exposure to air also led to a significant decrease in the yield of tellurides **4**. With powdered tellurium alone, no reaction took place.

The mechanism of this interesting telluration process has not yet been investigated, but the reaction may be depicted as an Ullmann-type condensation of a telluro analog (Scheme 1)[14]. Iodonitroarene **1** reacts with nascent copper(0) to produce arylcopper(I) com-

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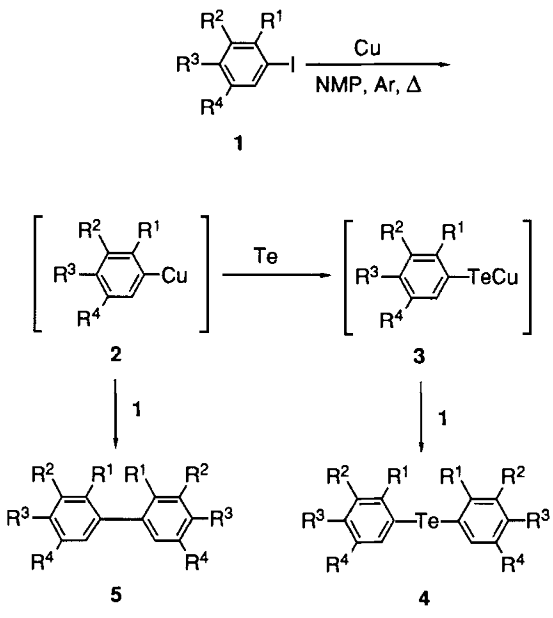
Scheme 1. Possible mechanism of the reaction of iodonitroarenes **1** with Te-Cu reagent



pound **2**, which would readily be converted to copper(I) aryl tellurolate **3** and further couple with another molecule of arene **1** to furnish the expected telluride **4**. In accord with this interpretation, 4-iodophenol and 4-iodobenzoic acid which do not undergo the Ullmann coupling reaction[13], failed to give the expected telluration products under the present reaction conditions.

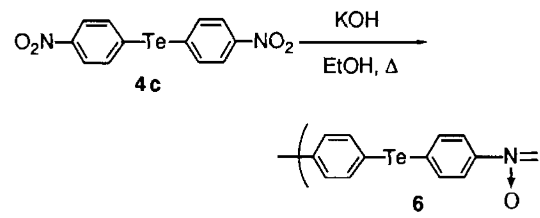
Nitroaryl telluride **4c** was gently heated with an excess of potassium hydroxide in dilute ethanolic solution to yield a reddish brown insoluble substance, which was approximately analyzed as $(C_{12}H_8N_2OTe)_n$, suggesting the formation of a multifunctional polymer **6** with a repeating unit $-C_6H_4-Te-C_6H_4-N(\rightarrow O)=N-$. Treatment of the same telluride with $LiAlH_4$ in dilute tetrahydrofuran (THF) solution also led to a dark red polymeric substance, which, however, failed to give a satisfactory analysis because of the presence of incombustible substance.

Table 1. Synthesis of diaryl tellurides **4**

	Iodoarene **1**				Conds.		Telluride **4**
	R¹	R²	R³	R⁴	Temp./°C	Time/h	Yield/%[a]
a	NO_2	H	H	H	100–110	1	83
b	H	NO_2	H	H	180–190	2	22
c	H	H	NO_2	H	150	5	63
					150	5	3[b]
					150	5	37[c]
					150	5	22[d]
d	Cl	H	NO_2	H	110–120	1.5	70
e	NO_2	H	Cl	H	130–140	4	51
f	NO_2	H	H	Cl	90–100	2	48[e]
g	MeO	H	NO_2	H	130–140	4	65
h	Me	H	NO_2	H	140–150	5	60
i	$(CH=CH)_2$		H	H	180–190	7	38–52

[a] Isolated yield. – [b] A combination of commercially obtained tellurium and copper powder was employed. – [c] Amount of the Te-Cu reagent was reduced to 1/2. – [d] *N,N*-Dimethylformamide was used as the solvent. – [e] 5,5′-Dichloro-2,2′-dinitrobiphenyl (**5f**) was obtained in 23% yield.

In summary, the Te-Cu couple generated in situ by the reaction of disodium telluride with copper(I) iodide in dry NMP has been found to be a convenient telluration reagent for some activated iodoarenes. Using this reagent system, we have prepared by a one-pot synthesis in satisfactory yields several bis(nitroaryl) tellurides **4**, which are otherwise laborious to obtain (Table 1).



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Experimental

Nitroaryl iodides were obtained either commercially or by the reaction of the nitroaryldiazonium salts with potassium iodide[15] and further purified by recrystallization. Sodium hydride (NaH; 60% dispersion in mineral oil) was washed with dry hexane prior to use. Tellurium (99.999%) and copper(I) iodide were used as commercially obtained. *N*-Methyl-2-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF) were distilled from calcium chloride and stored over 4-Å molecular sieves. – Melting points: Yanagimoto hot-plate apparatus, uncorrected. – ^1H NMR: in $CDCl_3$, Varian Gemini 200-MHz NMR spectrometer, tetramethylsilane as internal reference. – IR: KBr pellets, Shimadzu FTIR-8100S infrared spectrophotometer. – MS (EI): 70 eV, Shimadzu GCMS-QP2000A mass spectrometer.

Sodium Telluride was obtained either as a deep purple homogeneous solution by heating tellurium and NaH in a molar ratio of 1:2 in NMP at 100–110°C under argon or as a pale yellow chalky suspension by heating both reagents in the same ratio in DMF at 140°C.

Reaction of Iodonitroarenes **1** *with the Tellurium-Copper Reagent. – General Procedure:* Iodonitroarene **1** (2.0 mmol) was added in one portion to the black suspension of the tellurium-copper reagent prepared by heating sodium telluride (2.0 mmol) and copper(I) iodide (4.0 mmol) in NMP (6–8 ml) for a few minutes, and the resulting mixture was kept at an appropriate temperature range for several hours as shown in Table 1. The progress of the reaction was monitored by TLC. During the course of this period, the color of the reaction mixture gradually changed from black to yellow or red. After the reaction mixture had been cooled, ethyl acetate (10 ml) and subsequently water (5 ml) were added, and deposited tellurium was filtered off together with copper and copper iodide. The filtrate was partitioned twice between ethyl acetate (15 ml × 2) and water (15 ml × 2). The organic phases were separated, combined, dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was chromatographed over silica gel by using hexane/ethyl acetate (5 ≈ 10:1) as the eluent to give the corresponding telluride **4**.

Bis(2-nitrophenyl) Telluride (**4a**): Red crystals, m.p. 138–139°C (ref.[4] 140°C). – ^1H NMR ($CDCl_3$): $\delta = 8.2-8.3$ (m, 2H, aromatic H), 7.8–7.9 (m, 2H, aromatic H), 7.3–7.5 (m, 4H, aromatic H). – IR (KBr): $\tilde{\nu} = 1520$ cm^{-1} (NO_2), 1350 (NO_2), 1320, 1300, 790, 730. – MS, *m/z* (%): 374 (21) [M^+, Te = 130], 252 (15) [$M^+ - 2\text{-}NO_2C_6H_4$], 236 (11), 206 (17), 106 (100), 78 (63).

Bis(3-nitrophenyl) Telluride (**4b**): Yellow crystals, m.p. 75–76°C. – ^1H NMR ($CDCl_3$): $\delta = 8.5-8.6$ (m, 2H, aromatic H), 8.1–8.2 (m, 2H, aromatic H), 7.8–8.1 (m, 2H, aromatic H), 7.44 (dd, $J =$

7.9, 2H, aromatic H). − IR (KBr): $\tilde{\nu}$ = 1520 cm^{-1} (NO$_2$), 1340 (NO$_2$), 860, 730. − MS, *m/z* (%): 374 (74) [M$^+$, Te = 130], 252 (28) [M$^+$ − 3-NO$_2$C$_6$H$_4$], 206 (33), 152 (58), 76 (100). − $\mathrm{C_{12}H_8N_2O_4Te}$ (371.8): calcd. C 38.77, H 2.17, N 7.53; found C 39.46, H 2.12, N 7.66.

Bis(4-nitrophenyl) Telluride (**4c**): Yellow crystals, m.p. 178−180°C (ref.[4] 170−172°C). − ^{1}H NMR (CDCl$_3$): δ = 8.09 (d, *J* = 9.0, 4H, aromatic H), 7.83 (d, *J* = 9.0, 4H, aromatic H). − IR (KBr): $\tilde{\nu}$ = 1510 cm^{-1} (NO$_2$), 1340 (NO$_2$), 850, 730. − MS, *m/z* (%): 374 (97) [M$^+$, Te = 130], 206 (27) [M$^+$ − 4-NO$_2$C$_6$H$_4$, − NO$_2$], 152 (46), 76 (100). − $\mathrm{C_{12}H_8N_2O_4Te}$ (371.8): calcd. C 38.77, H 2.17, N 7.53; found C 38.87, H 2.16, N 7.48.

Bis(2-chloro-4-nitrophenyl) Telluride (**4d**): Yellow crystals, m.p. 157−159°C. − ^{1}H NMR (CDCl$_3$): δ = 8.33 (d, *J* = 2.3, 2H, aromatic H), 7.97 (dd, *J* = 8.5, 2.4, 2H, aromatic H), 7.66 (d, *J* = 8.5, 2H, aromatic H). − IR (KBr): $\tilde{\nu}$ = 1520 cm^{-1} (NO$_2$), 1340 (NO$_2$), 880, 760, 740. − MS, *m/z* (%): 442 (41) [M$^+$, Te = 130], 286 (17) [M$^+$ − ClNO$_2$C$_6$H$_3$], 240 (13), 75 (100). − $\mathrm{C_{12}H_6Cl_2N_2O_4Te}$ (440.8): calcd. C 32.71, H 1.37, N 6.35; found C 32.53, H 1.42, N 6.31.

Bis(4-chloro-2-nitrophenyl) Telluride (**4e**): Red crystals, m.p. 135−138°C. − ^{1}H NMR (CDCl$_3$): δ = 8.28 (d, *J* = 2.1, 2H, aromatic H), 7.73 (d, *J* = 8.4, 2H, aromatic H), 7.42 (dd, *J* = 8.4, 2.1, 2H, aromatic H). − IR (KBr): $\tilde{\nu}$ = 1510 cm^{-1} (NO$_2$), 1320 (NO$_2$), 1280, 1240, 880, 830, 760. − MS, *m/z* (%): 442 (29) [M$^+$, Te = 130], 286 (16) [M$^+$ − ClNO$_2$C$_6$H$_3$], 270 (17), 240 (23), 140 (100), 112 (55), 75 (71). − $\mathrm{C_{12}H_6Cl_2N_2O_4Te}$ (440.8): calcd. C 32.71, H 1.37, N 6.35; found C 32.90, H 1.36, N 6.36.

Bis(5-chloro-2-nitrophenyl) Telluride (**4f**): Red crystals, m.p. 167−170°C. − ^{1}H NMR (CDCl$_3$): δ = 8.26 (d, *J* = 8.9, 2H, aromatic H), 7.80 (d, *J* = 2.1, 2H, aromatic H), 7.48 (dd, *J* = 8.8, 2.2, 2H, aromatic H). − IR (KBr): $\tilde{\nu}$ = 1510 cm^{-1} (NO$_2$), 1490, 1330 (NO$_2$), 1320, 1290, 1100, 750. − MS, *m/z* (%): 442 (32) [M$^+$, Te = 130], 286 (24) [M$^+$ − ClNO$_2$C$_6$H$_3$], 270 (19), 240 (22), 140 (100), 112 (48), 75 (68). − $\mathrm{C_{12}H_6Cl_2N_2O_4Te}$ (440.8): calcd. C 32.71, H 1.37, N 6.35; found C 33.12, H 1.47, N 6.43.

Bis(2-methoxy-4-nitrophenyl) Telluride (**4g**): Yellow crystals, m.p. 180−183°C. − ^{1}H NMR (CDCl$_3$): δ = 7.5−7.8 (m, 6H, aromatic H), 3.99 (s, 6H, OCH$_3$). − IR (KBr): $\tilde{\nu}$ = 1520 cm^{-1} (NO$_2$), 1330 (NO$_2$), 1240, 1040, 870, 800, 740. − MS, *m/z* (%): 434 (100) [M$^+$, Te = 130], 106 (24), 76 (55). − $\mathrm{C_{14}H_{12}N_2O_6Te}$ (431.9): calcd. C 38.94, H 2.80, N 6.48; found C 39.30, H 3.01, N 6.41.

Bis(2-methyl-4-nitrophenyl) Telluride (**4h**): Yellow crystals, m.p. 127−130°C. − ^{1}H NMR (CDCl$_3$): δ = 8.13 (d, *J* = 2.5, 2H, aromatic H), 7.84 (dd, *J* = 8.4, 2.6, 2H, aromatic H), 7.59 (d, *J* = 8.4, 2H, aromatic H), 2.54 (s, 6H, CH$_3$). − IR (KBr): $\tilde{\nu}$ = 1520 cm^{-1} (NO$_2$), 1330 (NO$_2$), 800, 740. − MS, *m/z* (%): 402 (70) [M$^+$, Te = 130], 136 (100), 90 (84). − $\mathrm{C_{14}H_{12}N_2O_4Te}$ (399.9): calcd. C 42.05, H 3.02, N 7.00; found C 42.09, H 3.12, N 6.88.

Bis(1-naphthyl) Telluride (**4i**): Pale yellow crystals, m.p. 110−112°C (hexane/chloroform) and 105−107°C (ethanol) (ref.[4] 110°C[16]). − ^{1}H NMR (CDCl$_3$): δ = 6.9−8.2 (m, 14H, aromatic H). − IR (KBr): $\tilde{\nu}$ = 1550 cm^{-1} (C=C), 1500 (C=C), 1350, 1250, 950, 780, 770, 640. − MS, *m/z* (%): 384 (26) [M$^+$, Te = 130], 254 (56), 127 (100).

5,5'-Dichloro-2,2'-dinitrobiphenyl (**5f**): Pale yellow crystals, m.p. 180−182°C (ref.[17] 179−180°C). − ^{1}H NMR (CDCl$_3$): δ = 8.23 (d, *J* = 8.8, 2H, aromatic H), 7.59 (dd, *J* = 8.8, 2.1, 2H, aromatic H), 7.31 (d, *J* = 2.2, 2H, aromatic H). − IR (KBr): $\tilde{\nu}$ = 1530 cm^{-1} (NO$_2$), 1350 (NO$_2$), 1100, 900, 850, 760. − MS, *m/z* (%): 266 (100) [M$^+$, −NO$_2$], 236 (42), 203 (48), 173 (47), 140 (38), 75 (99). − $\mathrm{C_{12}H_6Cl_2N_2O_4}$ (313.2): calcd. C 46.02, H 1.93, N 8.94; found C 46.09, H 1.93, N 9.00.

Synthesis of Polymeric Telluride (**6**) *from Bis(4-nitrophenyl) Telluride* (**4c**): A mixture of **4c** (220 mg, 0.59 mmol), potassium hydroxide (500 mg, 8.9 mmol), and ethanol (7 ml) was heated under gentle reflux for 3 h to give a reddish brown precipitate, which was filtered off and washed successively with 10% hydrochloric acid (3 ml), water (30 ml), ethanol (20 ml), and ethyl acetate (30 ml). After drying, polymer **6** weighted 100 mg (52%). − IR (KBr): $\tilde{\nu}$ = 1470 cm^{-1}, 1450 ($\mathrm{N{=}N{\rightarrow}O}$), 1380 ($\mathrm{N{=}N{\rightarrow}O}$), 1330 ($\mathrm{N{=}N{\rightarrow}O}$), 1280, 1010, 820. − $(\mathrm{C_{12}H_8N_2OTe})_n$ $(323.8)_n$: calcd. C 44.51, H 2.49, N 8.65; found C 46.49, H 2.85, N 8.38.

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