Sodium Telluride in *N*-Methyl-2-pyrrolidone: An Efficient Telluration System for the Synthesis of Aromatic Tellurides and Ditellurides

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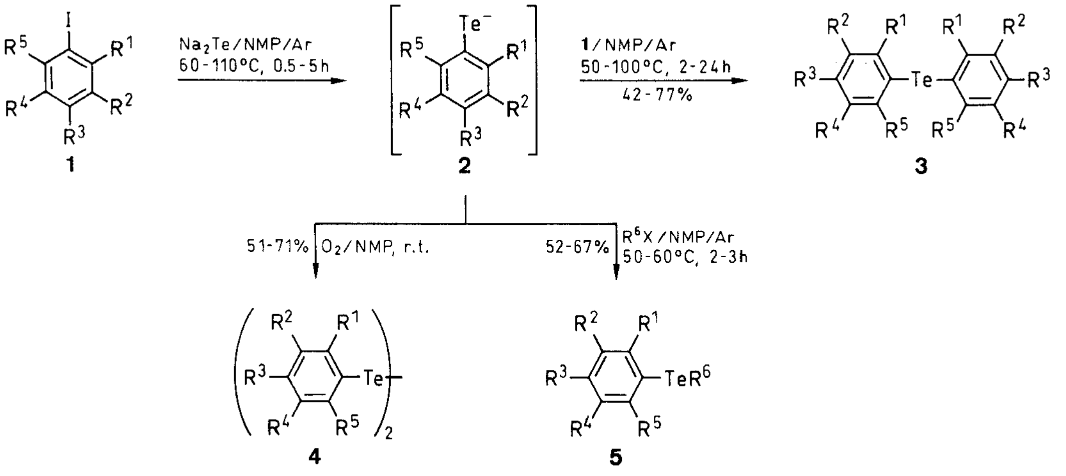
Sodium telluride prepared in situ from tellurium and sodium hydride in *N*-methyl-2-pyrrolidone was found to act as an efficient tellurating agent for nonactivated aromatic iodides, providing a simple route to a variety of diaryl tellurides, alkyl aryl tellurides and diaryl ditellurides.

Recently, aromatic tellurides and ditellurides are receiving considerable attention as organic reagents as well as starting materials for organic conductors and new imaging systems. Conventional preparative routes of aromatic tellurides involve the reaction of organometallic compounds with elemental tellurium or tellurium(IV) chloride,[1] reduction of diaryltellurium dihalides[1,2] or oxides,[3] treatment of diazotized aromatic amines with potassium tellurocyanide or sodium arenetellurolates,[4-6] and copper(I) or light-assisted reaction of aryl halides with sodium arenetellurolate.[7,8] Aromatic ditellurides are usually obtained by the reaction of organometallic reagents with elemental tellurium followed by air oxidation of the resulting arenetellurolates.[1] All of these procedures are, however, not free from some drawbacks: difficult availability of starting materials, toxicity or expense of reagent, low yields, lack of generality, tedious manipulation, need of special equipment, high dilution reaction, or concurrent formation of byproducts.

We have previously reported a convenient synthesis of symmetrical aromatic tellurides from nonactivated aromatic iodides.[9,10] Two types of the reagent systems employed therein were (i) tellurium and Rongalite ($HOCH_2SO_2Na$) in dilute aqueous alkali and (ii) tellurium and sodium hydride in dry dimethylformamide. Although both of these reagents worked satisfactorily with a wide variety of aromatic iodides, the yields of tellurides were often fair to modest due to the concurrent side reactions, especially the reductive dehalogenation in the former case and the formation of tellurocarbamates in the latter. During the attempts to suppress these undesirable side reactions, we were pleased to find that the use of *N*-methyl-2-pyrrolidone (NMP) as the solvent system could improve remarkably the yields of expected tellurides. Using this modified procedure, diaryl ditellurides and alkyl aryl tellurides could also be obtained in a one-pot way in good yields. It is the aim of the present paper to describe some details of our improvement and results obtained thereby.



1-4	R¹	R²	R³	R⁴	R⁵	1-4	R¹	R²	R³	R⁴	R⁵
a	H	H	H	H	H	**f**	$(CH{=}CH)_2$		H	H	H
b	Me	H	H	H	H	**g**	H	$(CH{=}CH)_2$		H	H
c	H	H	Me	H	H	**h**	Me	H	H	$(CH{=}CH)_2$	
d	H	H	OMe	H	H	**i**	F	F	F	F	F
e	Me	H	Me	H	Me						

1, 2, 5	R¹	R²	R³	R⁴	R⁵	R⁶
j	H	H	Me	H	H	*n*-C_7H_{15}
k	$-(CH{=}CH)_2-$		H	H	H	*n*-C_7H_{15}
l	H	$-(CH{=}CH)_2-$		H	H	Me

When finely ground tellurium was heated with sodium hydride in NMP in a molar ratio 1:2 at around 100-110 °C for 0.6-1.0 hours, there resulted a deep purple homogeneous solution of sodium telluride, which could be stored without appreciable change for many days under the exclusion of air. This is in marked contrast to the use of dimethylformamide as the solvent where sodium telluride was obtained as a pale yellow chalky suspension which slowly degraded on storage. Furthermore, heating at higher temperatures (up to 140 °C) was necessary to obtain the reagent in dimethylformamide. An aromatic iodide **1** (ArI) was added in small portions over 0.5-3 hours to the above prepared solution of sodium telluride, keeping an ArI/Te ratio within 1.1-1.5, and the resulting mixture was stirred at 50-100 °C for 8-24 hours. Telluration occurred smoothly and usual workup followed by chromatographic purification of the crude product gave the expected symmetrical diaryl telluride **3** in a good yield. Addition of aromatic iodide in one portion led to a significant decrease in yield. Aromatic bromides were much less reactive and chlorides remained intact under the conditions employed. The results of our experiments together with some physical properties of the tellurides and ditellurides obtained are summarized in Table 1.

When the reaction was carried out similarly with an ArI/Te ratio of 0.45–0.60, sodium arenetellurolate **2** was obtained. Dilution of this solution with benzene followed by aeration readily led to diaryl ditelluride **4** in a satisfactory yield. When the above solution of tellurolate **2** was heated with excess of an alkyl halide at 50–60 °C, alkyl aryl telluride **5** was obtained in 52–67% yields. Dialkyl telluride formed as byproduct was easily removed by chromatography over silica gel using hexane as the eluant.

Reductive dehalogenation was the major competing reaction which reduced the yields of tellurides appreciably. This side reaction was significant when sodium telluride prepared from tellurium and alkaline Rongalite was used. It was also important when the reactions were carried out in dimethylformamide, but the tendency decreased considerably in NMP. Another drawback using dimethylformamide as the solvent was the loss of the sodium telluride in the formation of tellurocarbamate **7**. The mechanism of the formation of this interesting byproduct is not investigated yet, but no carbamate analog could be observed with the reactions in NMP. Compari-

Table 1. Diaryl Tellurides **3a**–**i**, Alkyl Aryl Tellurides **5j**–**l**, and Diaryl Ditellurides **4a**, **4c**–**f** and **4h** Prepared

Product	Reaction Temp (°C), Time (h)	ArI/Te Ratio	Yield (%)[a]	mp (°C)[b] or bp (°C)/Torr	Molecular Formula[c] or Lit. mp/bp (°C)/Torr	MS (70 eV)[d] *m*/*z* (%)	IR (KBr)[e] ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS)[f] δ, *J* (Hz)
3a	60, 8	1.5	77	150–151/1.5	182–183/16.5[11]	284 (M^+, 26), 207 (32), 77 (100)	1570, 1470, 1430, 1060, 1020, 730, 690, 650	6.90–7.90 (m)
3b	70, 14	1.5	55	36–37	37–38[21]	312 (M^+, 44), 221 (18), 91 (100)	1580, 1460, 1450, 1380, 1020, 740	2.41 (s, 6H), 6.92–7.49 (m, 8H)
3c	70, 12	1.5	42	62–64	64–65[9]	312 (M^+, 53), 221 (11), 91 (100)	1480, 1380, 1300, 1200, 1180, 800	2.31 (s, 6H), 6.90 (d, 4H, *J* = 8.0), 7.50 (d, 4H, *J* = 8.0)
3d	80, 16	1.3	58	50–52	53–54[12]	344 (M^+, 43), 237 (20), 107 (100)	1580, 1480, 1440, 1280, 1240, 1170, 1030, 830, 810	3.60 (s, 6H), 6.61 (d, 4H, *J* = 7.0), 7.51 (d, 4H, *J* = 7.0)
3f	100, 21	1.1	76	123–126	126.5[13]	384 (M^+, 26), 254 (56), 127 (100)	1550, 1500, 1350, 1250, 950, 780, 770, 640	6.89–8.21 (m)
3g	100, 24	1.1	61	142–143	144–145[14]	384 (M^+, 18), 254 (100), 127 (43)	1610, 1570, 1470, 880, 810, 745, 730	6.95–8.22 (m)
3h	90, 20	1.5	53	142–143	142–144[10]	412 (M^+, 35), 267 (82), 141 (100)	1500, 1370, 1310, 820, 770, 740	2.44 (s, 6H), 7.08–8.42 (m, 12H)
3i	50, 2	1.5	56	49–50	50–51[15]	464 (M^+, 54), 297 (100)	1640, 1510, 1480, 1380, 1080, 970, 790	
4a	120, 5	0.49	66	64–65	66–67[16]	414 (M^+, 22), 207 (31), 77 (100)	1470, 1430, 1060, 990, 740, 690, 450	6.97–7.84 (m)
4c	110, 3	0.48	64	49–50	52[16]	442 (M^+, 10), 221 (25), 91 (100)	1540, 1480, 1010, 790, 480	2.37 (s, 6H), 7.00 (d, 4H, *J* = 8.1), 7.67 (d, 4H, *J* = 8.1)
4d	100, 7	0.50	57	53–54	56–58[17]	474 (M^+, 12), 237 (15), 107 (100)	1490, 1290, 1250, 1170, 1030, 810, 510	3.81 (s, 6H), 6.75 (d, 4H, *J* = 8.8), 7.70 (d, 4H, *J* = 8.8)
4e	120, 5	0.59	71	124–126	$C_{18}H_{22}Te_2$ (493.6)	498 (M^+, 11), 249 (16), 119 (100)	1560, 1540, 1460, 1370, 1290, 1030, 1010, 850, 840, 700	2.31 (s, 6H), 2.36 (s, 12H), 6.87 (s, 4H)
4f	90, 8	0.45	59	115–118	119–122[16]	514 (M^+, 13), 257 (44), 127 (100)	1500, 1250, 1130, 1020, 950, 790, 760, 640, 520	7.19–8.21 (m)
4h	110, 8	0.60	51	108–110	$C_{22}H_{18}Te_2$ (537.6)	542 (M^+, 6), 271 (6), 141 (100)	1540, 1500, 1460, 1420, 810, 770, 740, 520	2.48 (s, 6H), 7.05–8.15 (m, 12H)
5j	(120, 4)[g] 60, 2	0.48	63	oil	$C_{14}H_{22}Te$ (317.9)	320 (M^+, 16), 222 (17), 91 (100)	1490, 1460, 1010, 800	0.85–1.92 (m, 13H), 2.35 (s, 3H), 2.88 (t, 2H, *J* = 7.6), 7.03 (d, 2H, *J* = 8.0), 7.64 (d, 2H, *J* = 8.0)
5k	(110, 2)[g] 60, 3	0.45	52	oil	$C_{17}H_{22}Te$ (354.0)	356 (M^+, 15), 257 (14), 127 (100)	1560, 1500, 1380, 1020, 790, 770	0.75–1.87 (m, 13H), 2.93 (t, 2H, *J* = 7.5), 7.28–8.29 (m, 7H)
5l	(130, 4)[g] 50, 2	0.45	67	59–60	57–58[18]	272 (M^+, 47), 257 (51), 127 (100)	1560, 1540, 1510, 1460, 820, 740	2.27 (s, 3H), 7.36–8.26 (m, 7H)

[a] Yield of isolated product based on **1**. No attempts were made to optimize the yields.
[b] Uncorrected, measured with a Yanagimoto hot-plate apparatus.
[c] Satisfactory microanalyses obtained: C ±0.35, H ±0.30.
[d] Recorded on a Shimadzu GCMS-OP 2000 A Mass spectrometer.
[e] Recorded on a Shimadzu FTIR-8100 S Infrared spectrophotometer.
[f] Obtained on a Varian-Gemini 200 MHz NMR spectrometer.
[g] Condition used for the preparation of sodium arenetellurolate.

son was made for the preparations of diheptyl telluride and di-1-naphthyl telluride using dimethylformamide and NMP as the respective reaction media (Table 2).

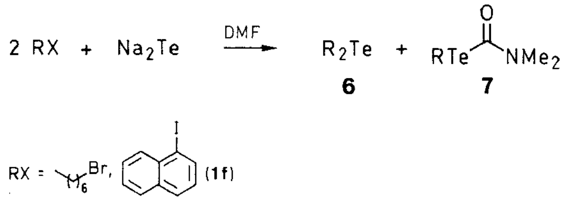


Table 2. The Effect of Solvent on Product Compositions

Halide	Solvent	Reaction Temp. (°C), Time (h)	RX/Te Ratio	Yield[a] (%) 6	7
n-$C_7H_{15}Br$	NMP	80, 15	2.1	68	0
	DMF	80, 15	2.1	43	10[b]
n-$C_{10}H_7I$ (**1f**)	NMP	100, 19	2.0	45 (**3f**)	0
	DMF	100, 19	2.0	32 (**3f**)	<1

[a] Yield of isolated product based on halide.

[b] Yellow oil: MS (DI): m/z (%) 301 (M^+, 100), 257 (33), 229 (21), 202 (9), 158 (31): IR (neat): ν = 1650, 1400, 1350, 1080, 890 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ = 0.78–0.84 (t, 3H, J = 5.5 Hz), 1.10–1.40 (m, 8H), 1.73–1.83 (m, 2H), 2.81 (s, 3H), 2.82–2.90 (t, 2H, J = 7.4 Hz), 2.98 (s, 3H).

		C	H	N	O
$C_{10}H_{21}NOTe$ (298.9)	calc.	40.19	7.08	4.68	5.35
	found	40.48	7.35	4.48	5.15

In summary, an improved procedure has been developed to provide diaryl tellurides **3**, alkyl aryl tellurides **5**, and diaryl ditellurides **4** from the same intermediate **2** in excellent yields. Major advantages as compared with the previous ones[9,10] are higher yields, stability and ease of handling of the reagent, and diminished side reaction.

Commercially non-available aryl iodides were prepared by the direct iodination of arenes with I_2/H_5IO_6[19] or by treatment of aryllithium with I_2.[20] NMP was made moisture-free by azeotropic distillation with benzene and stored over molecular sieves 4Å. NaH (60% dispersion in mineral oil) was washed with hexane prior to use. Tellurium (99.999%) was used as commercially obtained.

Di-(1-naphthyl) Telluride (3f); Typical Procedure:

1-Iodonaphthalene (**1f**; 310 mg, 1.2 mmol) was added in small portions over 1.5 h to a solution of Na_2Te (1.1 mmol) in NMP (3.5 mL) at 100 °C under an Ar atmosphere, and the resulting mixture was kept at this temperature for 19 h. During the course of this period, the color of the solution gradually changed from deep purple to black. The progress of the reaction was monitored by TLC. After complete disappearance of starting material, the reaction was quenched by the addition of sat. aq NH_4Cl (1 mL) followed by benzene (5 mL). The tellurium deposit was filtered off and the filtrate was partitioned between EtOAc (30 mL) and H_2O (20 mL). The organic phase was separated and dried (Na_2SO_4). The solvent was removed and the residue was chromatographed over silica gel using hexane as the solvent to give crude telluride **3f**, which was recrystallized from hexane/$CHCl_3$ (1 : 1) as yellow crystals; yield: 180 mg (76%).

		C	H
$C_{20}H_{14}Te$ (381.9)	calc.	62.90	3.69
	found	62.84	3.70

Diphenyl Ditelluride (4a); Typical Procedure:

Iodobenzene (**1a**; 130 mg, 0.64 mmol) was added dropwise to a stirred solution of Na_2Te (1.3 mmol) in NMP (4 mL) and the mixture was heated at 120 °C for 5 h. After cooling, the mixture was diluted with benzene (5 mL) and a stream of air was bubbled into the dark solution. Free tellurium which separated was removed by filtration and the filtrate was worked up as usual to give crude product ditelluride **4a**, which was purified by recrystallization from a mixture of hexane and EtOAc (3 : 1) to obtain pure product; yield: 90 mg (66%).

		C	H
$C_{12}H_{10}Te_2$ (409.4)	calc.	35.20	2.46
	found	35.28	2.48

Methyl 2-Naphthyl Telluride (5l); Typical Procedure:

Following the same procedure as described above, a solution of sodium naphthalene-2-tellurolate (**2l**) was prepared from Te (170 mg, 1.3 mmol), 2-iodonaphthalene (**1l**; 150 mg, 0.59 mmol) and NMP (4 mL). An excess of MeI (0.40 mL, 4.3 mmol) was then added and the resulting mixture was stirred at 50 °C for 2 h. Usual workup of the mixture gave methyl 2-naphthyl telluride (**5l**) as pale yellow crystals; yield: 110 mg (67%).

		C	H
$C_{11}H_{10}Te$ (269.8)	calc.	48.97	3.74
	found	48.77	3.71

(1) For a survey of these and other methods, see:
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