Synthesis of Symmetrical Polycyclic Aromatic Tellurides

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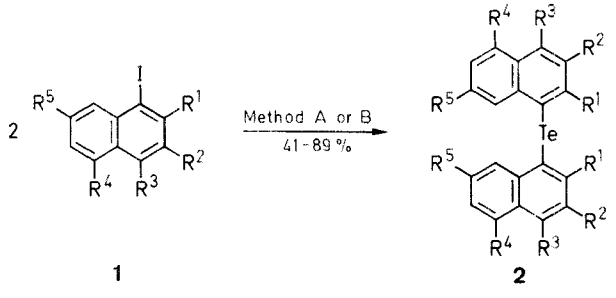
A direct synthesis of 13 polycyclic aromatic tellurides from the corresponding aromatic iodides has been achieved using sodium telluride, prepared by two different methods; (i) using tellurium and Rongalite $HOCH_2SO_2Na$ in dilute aqueous alkali, and (ii) from tellurium and sodium hydride in dry dimethylformamide. A comparison of these two types of tellurating agents has been made.

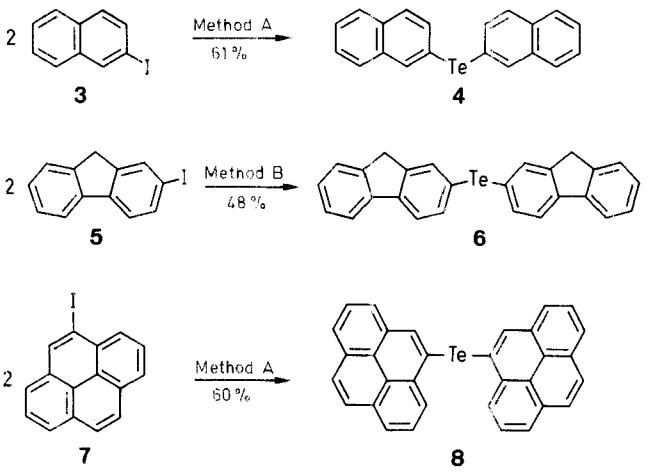
Aromatic tellurides are of considerable interest in connection with studies on organic conductors and new imaging systems. They are usually obtained by the reaction of organometallic compounds with elemental tellurium or tellurium tetrachloride,[1] reduction of diaryltellurium dihalides,[1,2] or oxides,[3] decomposition of diaryl ditellurides,[1] treatment of diazotized aromatic amines with sodium aryltellurolates[4] or potassium tellurocyanide,[5] copper(I) or light-assisted reaction of aryl halides with aryltellurolate anion,[6] and photostimulated reaction of aryl halides with sodium telluride.[7] However, most of these methods suffer from a limited scope for the preparation of polycyclic aromatic tellurides because of the difficult availability of starting materials, low yields, and concurrent formation of by-products.

Recently, in our laboratory a new, efficient method has been developed for the synthesis of symmetrically substituted diaryl tellurides in high yields from nonactivated aryl iodides using tellurium and Rongalite ($HOCH_2SO_2Na$) as the tellurating agent.[8] We wish now to report that this method (Method A)



Method A: Na_2Te/H_2O, 60°C
Method B: NaH/Te(→Na_2Te)/DMF, 140°C

works quite well with a variety of polycyclic aromatic iodides; polycyclic tellurides are obtained in good to moderate yields using sodium telluride, prepared from tellurium and Rongalite in dilute aqueous alkali under mild conditions, viz., at 60°C for 5–10 h (Table).



1, 2	R^1	R^2	R^3	R^4	R^5
a	H	H	H	H	H
b	CH_3	H	H	H	H
c	CH_3	CH_3	H	H	H
d	H	H	CH_3	H	H
e	H	H	OMe	H	H
f	H	H	F	H	H
g	H	*t*-C_4H_9	H	H	*t*-C_4H_9
h	H	H	CH_2CH_2		H
i	$(CH=CH)_2$		H	H	H
j	H	$(CH=CH)_2$		H	H

Table. Polycyclic Aromatic Tellurides **2a–j**, and **4**, **6**, and **8** Prepared

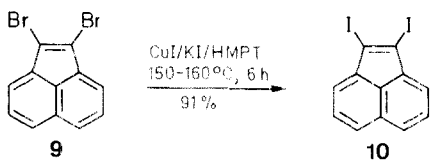
Product	Method	Yield[a] (%)	mp (°C)[b] (solvent)	Molecular Formula[c] or Lit. mp (°C)	IR (KBr)[d] ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS)[e] δ, J(Hz)
2a	A B	70 (18) 59 (36)	122–126 (*n*-hexane/$CHCl_3$)	126.5[14]	1540, 1490, 1380, 1240, 1195, 1015, 940, 780, 760	6.9–8.2 (m)
2b	B	48 (17)	142–144 (EtOH)	$C_{22}H_{18}Te$ (410.0)	1500, 1370, 1310, 820, 770, 740	2.42 (s, 6H); 7.1–8.4 (m, 12H)
2c	B	45 (25)	174–177 (EtOH)	$C_{24}H_{22}Te$ (438.0)	1490, 1425, 1250, 1160, 910, 885, 880, 845, 770, 750, 740	2.33 (s, 6H); 2.41 (s, 6H); 7.2–7.7 (m, 8H); 8.3–8.6 (m, 2H)
2d	B	47 (27)	122–124 (EtOH)	$C_{22}H_{18}Te$ (410.0)	1590, 1505, 1415, 1370, 1260, 1200, 980, 825, 750	2.64 (s, 6H); 6.9–8.2 (m, 12H)
2e	B	43 (27)	122–124 (benzene/*n*-hexane)	$C_{22}H_{18}O_2Te$ (442.0)	1570, 1485, 1435, 1395, 1355, 1300, 1250, 1230, 1105, 1070, 800, 790, 750, 740	3.93 (s, 6H); 6.57 (d, 2H, J = 7); 7.2–7.5 (m, 4H); 7.75 (d, 2H, J = 7); 8.0–8.3 (m, 4H)
2f	B	41 (19)	139–142 (EtOH)	$C_{20}H_{12}F_2Te$ (417.9)	1595, 1500, 1450, 1410, 1380, 1365, 1255, 1235, 1040, 830, 820, 755	6.7–8.2 (m)
2g	B	45 (18)	161–164 (benzene/*n*-hexane)	$C_{36}H_{46}Te$ (606.4)	1600, 1480, 1460, 1360, 885	1.15 (s, 18H); 1.19 (s, 18H); 7.2–8.1 (m, 10H)
2h	B	42 (23)	146–148 (benzene)	$C_{24}H_{18}Te$ (434.0)	1590, 1420, 1360, 845, 780	3.31 (s, 4H); 6.9–7.7 (m, 10H)
2i	A	89 (10)	258–260 (*n*-hexane/$CHCl_3$)	$C_{28}H_{18}Te$ (482.1)	1510, 1435, 1255, 890, 880, 840, 770, 730	7.1–7.5 (m, 4H); 7.6–8.0 (m, 2H); 8.2 (br s, 1H); 8.6–8.9 (m, 2H)
2j	A	55 (20)	208–212 (benzene/*n*-hexane)	$C_{28}H_{18}Te$ (482.1)	1480, 1440, 895, 885, 740, 730, 715	7.0–8.6 (m)
4	A	61 (18)	143–147 (benzene)	144–145[15]	1610, 1570, 1490, 850, 810, 745, 730	7.0–8.2 (m)
6	B	48 (8)	214–216 (benzene)	$C_{26}H_{18}Te$ (458.0)	1440, 1395, 1190, 1180, 1000, 955, 820, 760, 730	3.78 (s, 4H); 7.2–7.8 (m, 14H)
8	A	60 (34)	216–221 (benzene)	$C_{32}H_{18}Te$ (530.1)	1580, 845, 815, 750, 710	7.5–8.5 (m)

[a] Yields refer to the isolated compounds and are not optimized. Numerals in parentheses refer to the parent hydrocarbon isolated.
[b] All melting points were determined on a hot-stage apparatus and are uncorrected.
[c] All new compounds gave satisfactory microanalyses: C ± 0.4, H ± 0.3; except for **8** (C + 0.6).
[d] Recorded as KBr pellet on a Hitachi 260-10 spectrophotometer.
[e] Recorded on JEOL-HM 60 and Hitachi R-600 spectrometers.

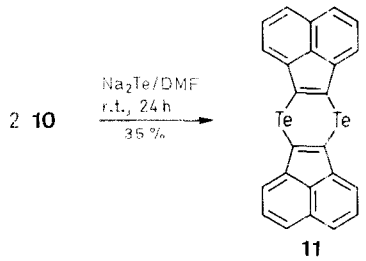
The reaction was clean and the only by-product was easily separable hydrocarbon, resulting from reductive dehalogenation of aryl iodide. Ditelluride, which usually accompanies the reaction of organometallic compound with tellurium, was not detected under our conditions. The reaction of non-activated aromatic halides with sodium telluride was only recently reported,[7,9] where the tellurating agent used was obtained by reacting directly sodium metal with tellurium, and the yields of diaryl tellurides range between 17–35%. Few polycyclic aromatic tellurides have so far been described in the literature and their chemistry remains unexplored.

Sodium telluride used in the present work (Method A) was a yellow powdery mixture with sodium sulfite, which was obtained by evaporating a wine-colored aqueous solution (see experimental) to dryness under reduced pressure.[8] Since the preparation of this reagent was felt to be a bit time-consuming and probably suggests an incomplete reduction of Te to Te^{2-}, we next turned to a suspension of sodium telluride in dimethylformamide (DMF), more easily obtained from the reaction of sodium hydride with tellurium in hot dimethylformamide. With this reagent (Method B), however, it was found that the reaction did not go to completion even after 24 h at 130°C, and the tellurides were isolated only in moderate yields. Efforts to increase the yield by using an excess of the reagent led to a mixture of telluride and ditelluride, inseparable by both crystallization and chromatography, as indicated by elemental analyses. This finding is in accordance with our previous observation that sodium telluride prepared from tellurium and Rongalite appeared to be more efficient in telluration of aromatic iodides than that obtained by reacting directly metallic sodium with tellurium.[8] The reason for the difference in apparent reactivity is not clear at present, since a simple combination with anhydrous sodium sulfite did not show any positive effect. Attempts to obtain unsymmetrical diaryl tellurides by reacting sodium telluride stepwise with two different polycyclic aromatic iodides were not entirely successful; addition of the first component to sodium telluride in dry dimethylformamide at 60°C followed by the second component with an interval of several hours led to a mixture of two symmetrical and one unsymmetrical products. Due to the weak bond character of tellurium to carbon, redistribution of the primary product should have occurred easily.

With a view to synthesize aromatic tellurides of interesting structures, telluration was tried under aprotic conditions with 9,10-diiodoanthracene and 1,2-diiodoacenaphthalene (**10**). The former gave a highly complex reaction mixture, but from the latter the desired cyclic bis-telluride **11** was obtained as red crystals by carrying out the reaction at room temperature.



9 10



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Although the overall reaction is formally double nucleophilic aromatic substitution, the results obtained, together with the behavior of other haloaryl compounds toward telluride anion, are suggestive of the $S_{RN}1$ mechanism.[10] Reductive dehalogenation, which always accompanies the telluration process, may well be accounted for by this reaction mechanism. Thus, in the case of 9-iodo-10-phenylanthracene, which can give rise to a stabilized radical intermediate, attempted telluration resulted only in the isolation of phenylanthracene.

Condensed polycylic aromatic iodides are not directly accessible by known iodination procedures because of the low oxidation potentials of substrates. However, they are easily obtained by the halogen exchange reaction using potassium iodide, copper(I) iodide, and aromatic bromides in hexamethylphosphoric triamide (HMPT).[11] Thus, a combination of halogen exchange reaction and telluration using sodium telluride provides an easy general access to various polycyclic aromatic tellurides.

In summary a simple one-pot synthesis of symmetrical polycyclic aromatic tellurides is reported, which gives products in yields better than those obtained by any indirect procedures previously reported in the literature.

Polycyclic Aromatic Tellurides; General Procedure:

Method A, *Using Te and Rongalite*: A mixture of powdered Te (128 mg, 1.0 mmol), $HOCH_2SO_2Na \cdot 2H_2O$ (339 mg, 2.2 mmol), and 5 N NaOH (1 mL) is stirred at 60°C for 2 h under N_2 to form Na_2Te as a wine-colored solution, which is evaporated to dryness under reduced pressure. To the yellow residue, a solution of aryl iodide (2.0 mmol) in dry DMF (3 mL) is added, and the mixture is stirred at 60°C for 10 h. The reaction is quenched wit 10% $(NH_4)_2SO_4$ (10 mL) and extracted with ether (10 mL). The ethereal extract is washed with water, dried (Na_2SO_4), and evaporated to give the crude telluride. This is purified by column chromatography on silica gel eluting with *n*-hexane (Table).

Method B, *Using Te and NaH in DMF*: A mixture of Te (128 mg, 1.0 mmol), NaH (53 mg, 2.2 mmol; 60% suspension in oil washed thoroughly with dry *n*-hexane to remove the mineral oil), and dry DMF (3 mL) is heated at 140°C for 1 h. The deep red color developed initially faded and changed to a pale yellow suspension within 0.5 h. This is cooled to room temperature and a solution of aromatic iodide (2.0 mmol) in dry DMF (3 mL) is added. The mixture is heated to 130°C and kept at this temperature for 24 h. The mixture is cooled to room temperature, and the telluride is isolated following the same procedure as described in Method A (Table).

1,2-Diiodoacenaphthalene (10):

A mixture of 1,2-dibromoacenaphthalene (0.31 g, 1 mmol),[12] CuI (1.90 g, 10 mmol), KI (3.32 g, 20 mmol), and HMPT (5 mL) is stirred for 6 h at 150–160°C. The progress of the reaction is monitored by GC. The reaction is quenched by the addition of 10% HCl (50 mL) followed by benzene (30 mL), and the resulting mixture is freed from insoluble copper(I) salt by filtration. The organic phase is separated, washed with 10% $NaHSO_3$ (10 mL), and filtered to remove the solid precipitated. Finally the organic layer is washed with water (25 mL) and dried (Na_2SO_4). The solvent is removed under reduced pressure to leave a solid which is purified by chromatography over silica gel using *n*-hexane as solvent and subsequently recrystallized from *n*-pentane to give pure iodide; yield: 0.367 g (91%); mp 147–149°C (Lit.[13] mp 136–137°C).

$C_{12}H_6I_2$ (404.0) calc. C 35.68 H 1.50
found 35.86 1.42

IR (NaCl): ν = 1490, 1460, 1180, 1140, 820, 770, 620, 570 cm^{-1}.

^1H-NMR (CCl_4): δ = 7.3–7.8 (m).

MS (70 eV): *m/z* (%) = 404 (M^+, 100); 277 (12); 150 (70); 100 (3); 98 (1).

Diacenaphtho[1,2-*b*:1′,2′-*e*][1,4]ditellurin (11):

To a suspension of Na_2Te (348 mg, 2.0 mmol) in dry DMF (5 mL) at room temperature, a solution of **10** (808 mg, 2.0 mmol) in DMF (3 mL) is added in one portion. The resulting mixture is stirred as such for 24 h and then worked up as described in Method A. The product is isolated by column chromatography on silica gel using benzene as eluent; yield: 195 mg (35%); mp 283–287°C (benzene).

$C_{24}H_{12}Te_2$	calc.	C 51.88	H 2.17
(555.6)	found	51.98	2.06

IR (KBr): ν = 1480, 1455, 1430, 1170, 1130, 1040, 820, 760 cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 7.2–7.8 (m).

MS (70 eV): m/z (%) = 556 (M^+, 28); 430 (96); 298 (77); 150 (100).

The authors wish to thank Dr. Kurt Loening, Nomenclature Director of Chemical Abstracts Service for assisting in naming the cyclic bis-telluride **11**. *One of us (S.P.) thanks the Ministry of Education, Science and Culture, Japan for a scholarship.*

Received: 5 December 1988

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