Journal of Organometallic Chemistry, 199 (1980) 377—387
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

TELLURIUM IN ORGANIC SYNTHESIS

X *. SYNTHESIS OF 3-HALOGENOBENZO[*b*]TELLUROPHENE DERIVATIVES

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(Received May 7th, 1980)

Summary

Several substituted 3-halogenobenzo[*b*]tellurophenes have been synthesized by treating phenylacetylenes with TeO_2 in acetic acid in the presence of a lithium halide. A mechanism is postulated involving an electrophilic attack by a solubilized tellurium species on the acetylenic bond with introduction of a halogen atom followed by cyclization to the benzo[*b*]tellurophene system. The benzo[*b*]tellurophenes can be easily chlorinated with Cl_2 gas to yield benzo[*b*]-tellurophene 1,1-dichloride derivatives, but attempted lithiation is the 3-position was unsuccessful and resulted in a ring rupture. When refluxed in trifluoroacetic acid 3-chlorobenzo[*b*]tellurophene was converted into 3-oxo-2,3-dihydrobenzo[*b*]tellurophene.

Introduction

Since the first synthesis of benzo[*b*]tellurophene in 1971 [1], a number of 2- and 3-functionalized derivatives have been synthesized by multi-step procedures [2,3]. The only halogen-substituted derivatives described in the literature were 3-chloro-2-phenylbenzo[*b*]tellurophene (1) [4], obtained from the 1 : 1 adduct of $TeCl_4$ and diphenylacetylene (2a) [5] by heating in trichlorobenzene, and 3-chloro- and 3-bromobenzo[*b*]tellurophene (4a, 4b) obtained from 3-oxo-2,3-dihydrobenzo[*b*]tellurophene (3) [6], which in turn was obtained by a lengthy procedure.

We recently reported, in a short communication [7], the synthesis of benzo-

* For part IX see ref. 24.

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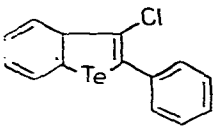

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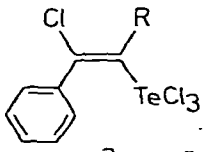
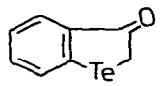


2 a R= C_6H_5

b R= H



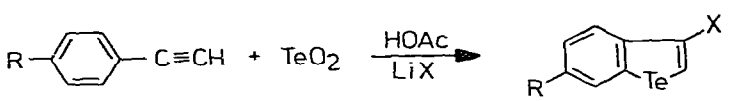
3

[*b*]tellurophene derivatives from tellurium dioxide, TeO_2, and various phenylacetylenes. In this paper we present the full experimental details for this reaction together with some new results.

Results and discussion

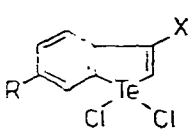
Benzo[*b*]tellurophenes 4 were formed in 21—92% yield, according to Scheme 1, when tellurium dioxide was refluxed in acetic acid with a suitable phenylacetylene for 20—48 h in the presence of a lithium halide, LiX. The reaction did not work with lithium fluoride, LiF. All compounds were isolated as their 1,1-dichlorides (5), obtained by passing chlorine through a CCl_4/petroleum ether solution of the benzo[*b*]tellurophenes 4 (after aqueous work-up, neutralization of the HOAc and ether extraction). The benzo[*b*]tellurophene 1,1-dichlorides were easily reduced, in almost quantitative yield with aqueous $Na_2S_2O_5$ to the parent compounds 4. The ^1H NMR spectra of compounds 4a and 4b were identical with those recorded for 3-chloro- and 3-bromobenzo[*b*]-tellurophene obtained by treating compound 3 with CCl_4 and CBr_4, respectively, in the presence of $(C_6H_5)_3P$ [6].

Scheme 1

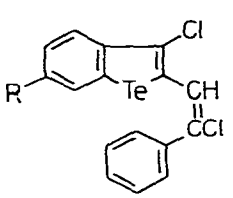


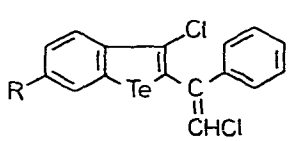
4 a R=H , X=Cl
b R=H , X=Br
c R=H , X=J
d R=CH_3 , X=Cl
e R=Br , X=Cl

In the three reactions according to Scheme 1 in which LiCl was used as the halide source, a by-product was isolated as a crystalline compound in a yield strongly dependent on the concentration of LiCl. The ^1H NMR spectrum indicated that the proton in the 2-position of the benzo[*b*]tellurophene system was

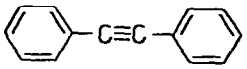


5 a R=H , X=Cl
b R=H , X=Br
c R=H , X=J
d R=CH_3 , X=Cl
e R=Br , X=Cl





6 a R=H
b R=CH_3
c R=Br



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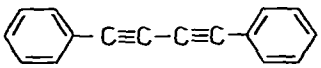

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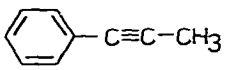

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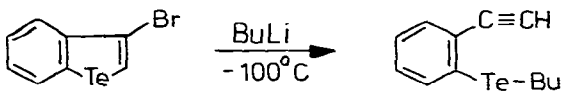
no longer present (this proton was clearly resolved in compounds 4a—4e). The mass spectrum indicated that a chlorinated phenylacetylene species (e.g. $C_6H_5C^+{=}CHCl$) had been added to the benzo[*b*]tellurophene system and we therefore suggest that this product has one of the two structures **6**. When compound **6a** was treated with Cl_2 gas it was converted into the corresponding benzo[*b*]tellurophene 1,1-dichloride (**7**). Diphenylacetylene (**8**) and diphenyldiacetylene (**9**) failed to react according to Scheme 1 indicating that certain steric demands must be fulfilled for the reaction to occur. The less bulky 1-phenyl-1-propyne (**10**) gave the expected products **11a** and **11b** in 49 and 28% yield, respectively, isolated as their dichlorides **12a** and **12b**.

If the compounds **4** could be metallated in the 3-position, they would probably serve as excellent starting materials for a variety of 3-substituted benzo[*b*]tellurophenes. However, when treated with BuLi even at —100° C in ether, compound **4b** was ring-opened to the acetylenic compound **13** in 71% yield according to Scheme 2, a reaction which was independently studied by Talbot

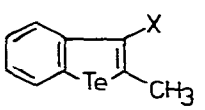
Scheme 2



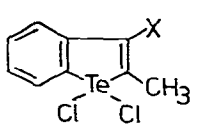
13

[6]. Such reactions are well documented in the selenophene series [8] and the selenium analogue of **13** has been obtained similarly [9]. This reaction may proceed either by lithiation in the 3-position followed by ring-opening and alkylation by butyl bromide, or by direct attack on the tellurium atom with elimination of LiBr. Phenyllithium failed to ring-open compound **4b** even at room temperature so we have not yet been able to distinguish between the two mechanisms. All attempts to prepare the corresponding Grignard reagent from compound **4b** have been unsuccessful.

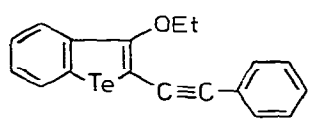
When compound **6a** was treated with sodium ethoxide in refluxing ethanol, a yellow oil was isolated in 59% yield. The IR spectrum clearly indicated an acetylenic compound and the mass spectrum and the ^1H NMR spectrum indicated that both chlorine atoms were absent from the molecule, one of them eliminated as HCl, the other one replaced by ethoxide. We therefore suggest structure **14** for this compound. This experiment, however, can not distinguish



11 a X=Br
b X=Cl



12 a X=Br
b X=Cl

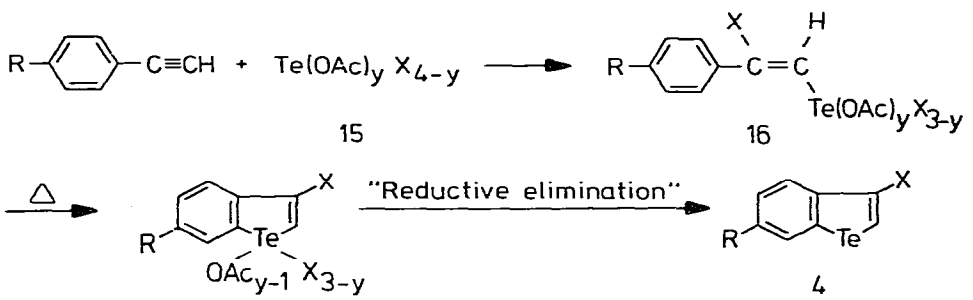


14

between the two structures suggested for compound **6** because they can both be converted to compound **14**, the first one by substitution of ethoxide followed by elimination of HCl, the second by substitution of ethoxide followed by a Fritch-Buttenberg-Wiechell rearrangement [10,11], a reaction which may take place under these reaction conditions.

We described in an earlier paper [12], the acetoxymethylation of some aromatic compounds with TeO_2/HOAc in the presence of LiBr. In those reactions TeO_2 serves merely as an oxidizing agent for acetic acid. In the present case TeO_2 dissolved by interaction with LiX adds to the triple bond of the phenylacetylene with introduction of a halogen atom (Scheme 3). The exact structure

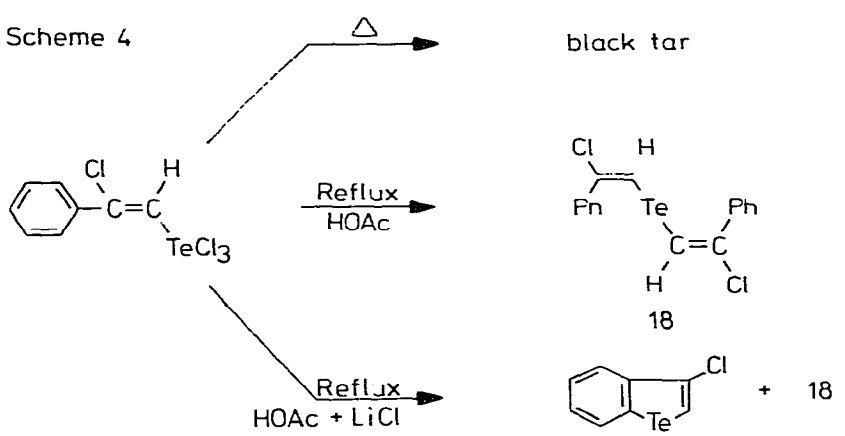
Scheme 3



of the attacking species is as yet unknown but halogen atoms and acetoxy groups are probably bonded to tellurium as in the general structure **15**. The primary product **16** is then cyclized to the benzo[*b*]tellurophene system **17**, probably by loss of HOAc (cf. the high reactivity of $Hg(OAc)_2$ compared with $HgCl_2$ towards aromatics) [13]. The last step in the reaction sequence must be formally a reductive elimination yielding compounds of type **4**.

When heated, 2-chloro-2-phenylvinyltellurium trichloride (**2b**) was reported to give only black tars and no cyclized product [14]. When refluxed in acetic acid, compound **2b** was converted into bis(2-chloro-2-phenylvinyl)telluride (**18**) [5]. We have found that compound **2b**, when heated in acetic acid in the presence of LiCl, can be converted into a mixture of 3-chlorobenzo[*b*]tellurophene (**4a**) and telluride **18** (Scheme 4). Recent results indicate [15] that the 1 : 1

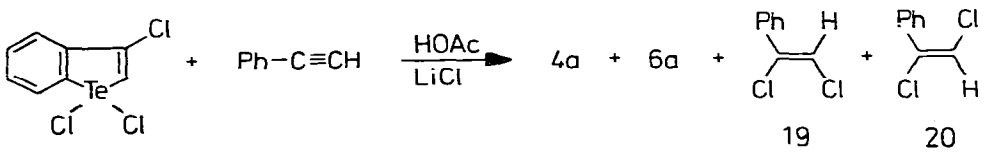
Scheme 4



adduct of $TeCl_4$ and phenylacetylene (2b) has the (*Z*)-configuration rather than the expected (*E*)-configuration. Clearly, in acetic acid solution in the presence of a lithium halide there must exist a pathway for interconversion of the two forms, allowing formation of compounds 4.

In order to cast some light upon the reductive elimination mentioned in Scheme 3, 3-chlorobenzo[*b*]tellurophene 1,1-dichloride (5a) was refluxed with phenylacetylene in acetic acid for 24 h in the presence of LiCl. The product mixture contained 3-chlorobenzo[*b*]tellurophene (4a) together with the two possible isomers of dichlorinated phenylacetylene (19, 20) and a small amount of compound 6a which crystallized upon cooling. (Scheme 5). Amongst the

Scheme 5



two dichlorinated phenylacetylenes the (*Z*)-isomer clearly predominated (*E*/*Z* = 5/95) as revealed by comparison with authentic samples [16,17]. Similar (*Z*)-chlorinations have been effected with antimony pentachloride [18], and the very high stereospecificity can be explained assuming a concerted addition as depicted in Fig. 1.

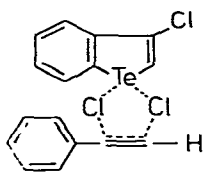
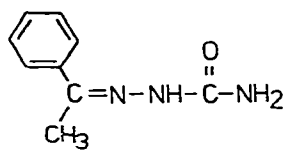


Fig. 1.

It is well-known, [19] that certain semicarbazones can be converted into acetylenic compounds when treated with selenium dioxide, and we thought that tellurium dioxide might also effect this transformation. When treated in acetic acid with TeO_2 in the presence of LiBr, acetophenone semicarbazone (21) was converted into 3-bromobenzo[*b*]tellurophene (4b), probably via phenylacetylene. However, the yield was low (9%) and the reaction could not be extended to other ketones.



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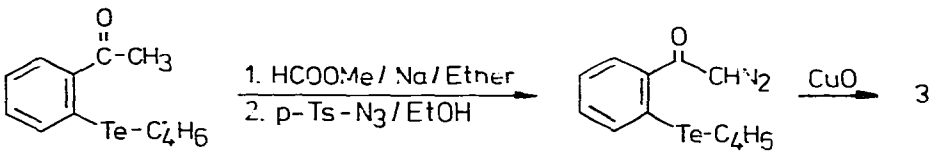
When 3-chlorobenzo[*b*]tellurophene (4a) was dissolved in trifluoroacetic acid the solution immediately turned deep purple, and after a few hours of reflux 3-oxo-2,3-dihydrobenzo[*b*]tellurophene (3) was isolated in 84% yield. The compound was identical in all respects with a sample prepared according to Scheme 6 [23]. 3-Bromobenzo[*b*]tellurophene (4b) did not give a purple

Scheme 6



colour and only 7% of compound **3** was isolated. 3-Chloro-2-methylbenzo[*b*]-tellurophene (**11b**) gave a purple colour when refluxed in trifluoroacetic acid, but work-up afforded only unchanged starting material. The transformation (**4a** → **3**) can be explained as outlined in Scheme 7. The low reactivity of the

Scheme 7

22a 22b

bromo-derivative **4b** can then be attributed to less favoured resonance stabilization of the carbonium ion intermediate, since the bromine analogue of compound **22b** would make an insignificant contribution.

Experimental

Materials and spectroscopic measurements

TeO_2 was obtained from PCR Research Chemicals, Inc. Phenylacetylene was a Fluka product and 1-phenyl-1-propyne was obtained from Aldrich. 4-Methylphenylacetylene [20], 4-bromophenylacetylene [20], diphenylacetylene [21] and diphenyldiacetylene [22] were synthesized by published methods. NMR spectra were recorded on a Bruker WP 200 instrument. Infrared spectra were obtained on a Perkin Elmer 257 instrument. Mass spectra were recorded with an LKB 9000 mass spectrometer. All melting points are uncorrected.

3-Chlorobenzo[b]tellurophene 1,1-dichloride (5a). Phenylacetylene (2.0 g, 19.6 mmol), TeO_2 (1.0 g, 6.3 mmol) and LiCl (1.2 g, 28.3 mmol) were refluxed in acetic acid (50 ml) for 45 h. Filtration and cooling separated 0.15 g, 6% yield, of compound **6a**, m.p. 138—39°C (acetonitrile). ^1H NMR ($CDCl_3$, Me_4Si) δ 7.25—8.10 ppm (several peaks) ^{13}C NMR ($CDCl_3$, Me_4Si) δ 123.05, 123.91, 125.92, 126.30, 126.78, 127.16, 128.64, 129.29, 129.38, 130.95, 131.18, 133.81, 138.05, 142.25 ppm. Mass spectrum: *m/e* (rel. intensity, *m/e* > 100, only peaks stronger than 10% of the base peak) 404(40), 402(80), 400(64), 398(32), 366(36), 364(32), 362(18), 332(40), 330(38), 328(24), 236(32), 202(100), 201(36), 200(52), 102(22). IR (KBr): 1495w, 1480m, 1445w, 1435w, 1250w, 925m, 905m, 845w, 755m, 750s, 710w, 680m cm^{-1}. The acetic acid solution was poured into ethyl ether (150 ml) and neutralized with $NaHCO_3$ (5% aq.). Drying ($CaCl_2$) of the organic layer and evaporation yielded a brown oil, which was dissolved in a mixture of CCl_4 (20 ml) and petroleum ether b.p. 40—60°C (10 ml). Careful bubbling of Cl_2 gas through this solution caused precipitation of compound **5a** as a yellow solid, 1.1 g, 52% yield. M.p.

275—280°C dec. (acetonitrile). Mass spectrum: *m/e* (rel. intensity, $m/e > 100$, only peaks stronger than 5% of the base peak) 269(25), 266(100), 264(81), 262(48), 261(18), 260(12), 258(6), 231(19), 229(18), 227(11), 226(5), 138(27), 137(8), 136(81), 130(11), 128(11), 126(6), 102(6), 101(69). IR (KBr): 3100m, 1570w, 1530s, 1435w, 1250m, 1095m, 920m, 765s, 725w, 710m cm^{-1}.

3-Chlorobenzo[b]tellurophene (4a). An ether suspension of the dichloride **5a** was shaken thoroughly with $Na_2S_2O_5$ (5% aq.) until all the material had dissolved. Drying ($CaCl_2$) and evaporation of the organic layer yielded compound **4a** as an oil in almost quantitative yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 7.26 (1H, t, J = 7.5 Hz), 7.47 (1H, t, J = 7.6 Hz), 7.89 (1H, d, J = 7.9 Hz), 7.95 (1H, d, J = 8.0 Hz), 8.40 ppm (1H, s). IR (neat:) 3090w, 3050w, 1445w, 1420m, 1280m, 1250m, 1020w, 915m, 760s, 715m, 680w, 655w cm^{-1}.

1,1-Dichloride of compound 6a (7). Compound **6a** was dissolved in CH_2Cl_2 and Cl_2 gas was bubbled through it for a few minutes. Addition of petroleum ether to give a cloudiness and cooling to —15°C separated yellow crystals of compound **7**, m.p. 269—270°C. IR (KBr): 1570w, 1560(w), 1510m, 1485w, 1450w, 1440m, 1220m, 930s, 900m, 840m, 760s, 690w, 680m cm^{-1}.

3-Bromobenzo[b]tellurophene 1,1-dichloride (5b). Phenylacetylene (2.0 g, 19.6 mmol), TeO_2 (1.0 g, 6.3 mmol) and LiBr (2.0 g, 23.0 mmol) were refluxed in acetic acid (50 ml) for 20 h, cooled to room temperature and poured into ethyl ether (150 ml) and neutralized with $NaHCO_3$ (5% aq.). Drying ($CaCl_2$) of the organic phase and evaporation yielded a brown oil, which was dissolved in a mixture of CCl_4 (30 ml) and petroleum ether b.p. 40—60°C (10 ml). Careful bubbling of Cl_2 gas through this solution caused precipitation of compound **5b** as a yellow solid, 2.2 g, 92% yield. M.p. 263—265°C (acetonitrile). IR (KBr): 3100m, 1530m, 1445w, 1435w, 1240m, 1095m, 890m, 880w, 765s, 735w, 705m cm^{-1}.

3-Bromobenzo[b]tellurophene (4b). An ether suspension of the dichloride **5b** was shaken thoroughly with $Na_2S_2O_5$ (5% aq.) until all material had dissolved. Drying ($CaCl_2$) and evaporation of the organic phase yielded compound **4b** as an oil in almost quantitative yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 7.21 (1H, t, J = 7.5 Hz), 7.44 (1H, t, J = 7.4 Hz), 7.89 (1H, d, J = 7.9 Hz), 7.96 (1H, d, J = 8.0 Hz), 8.60 ppm (1H, s). Mass spectrum: *m/e* (rel. intensity, $m/e \geq 100$, only peaks stronger than 10% of the base peak) 312(47), 310(84), 308(70), 307(26), 306(35), 231(56), 229(53), 227(32), 226(14), 130(14), 128(15), 102(15), 101(100), 100(13). IR (neat): 3080w, 1440m, 1420m, 1225s, 1100w, 1020m, 880m, 760s, 710m, 700m, 640w cm^{-1}.

3-Iodobenzo[b]tellurophene 1,1-dichloride (5c). Phenylacetylene (2.0 g, 19.6 mmol) TeO_2 (1.0 g, 6.3 mmol) and LiI (3.2 g, 23.9 mmol) were refluxed in acetic acid (50 ml) for 20 h, cooled to room temperature and poured into ethyl ether (150 ml) and neutralized with $NaHCO_3$ (5% aq.). Drying ($CaCl_2$) of the organic phase and evaporation yielded a dark oil which was dissolved in a mixture of CCl_4 (10 ml) and petroleum ether b.p. 40—60°C (10 ml) and cooled to —50°C. Careful bubbling of Cl_2 gas through this solution caused precipitation of compound **5c** as a semi-solid 0.55 g, 21% yield, which could be crystallized from acetonitrile, m.p. 260—261°C. IR (KBr): 3080m, 1515m, 1440w, 1230w, 1095m, 870m, 760s, 700m cm^{-1}.

3-Iodobenzo[b]tellurophene (4c). An ether suspension of the dichloride **5c** was shaken thoroughly with $Na_2S_2O_5$ (5% aq.) until all material had dissolved. Drying ($CaCl_2$) and evaporation of the organic phase yielded compound **4c** an oil in almost quantitative yield. ^1H NMR ($CHCl_3$, Me_4Si) δ 7.21 (1H, t, J = 7.5 Hz), 7.48 (1H, t, J = 7.4 Hz), 7.95 (1H, d, J = 7.9 Hz), 7.98 (1H, d, J = 8.0 Hz), 9.00 ppm (1H, s). Mass spectrum: *m/e* (rel. intensity, *m/e* > 100, only peaks stronger than 10% of the base peak) 358(15), 356(14), 231(10), 229(12), 156(10), 141(37), 139(100), 113(11), 111(31), 102(11), 101(16). IR (neat): 3080w, 3040w, 1440m, 1425m, 1410w, 1245m, 1100w, 1020m, 865m, 760s, 710m, 660w cm^{-1}.

3-Chloro-6-methylbenzo[b]tellurophene 1,1-dichloride (5d). 4-Methylphenylacetylene (2.0 g, 17.2 mmol), TeO_2 (1.0 g, 6.3 mmol) and LiCl (1.2 g, 28.3 mmol) were refluxed in acetic acid (50 ml) for 48 h. Filtration and cooling separated 0.10 g, 4.0% yield, of compound **6b**, m.p. 188—189° C (acetonitrile). Mass spectrum: *m/e* (rel. intensity, *m/e* > 100, only peaks stronger than 20% of the base peak) 432(50), 430(100), 428(80), 426(48), 396(24), 394(64), 392(54), 390(34), 360(58), 358(56), 356(36), 230(80), 229(60), 228(40), 215(40), 213(30). IR (KBr): 1510w, 1475m, 1250m, 1180w, 1135w, 1020w, 930m, 905m, 870w, 850w, 815s, 805s, 675w, 635w cm^{-1}.

The acetic acid solution was poured into ethyl ether (150 ml) and neutralized with $NaHCO_3$ (5% aq.). Drying ($CaCl_2$) of the organic phase and evaporation yielded a brown oil which was dissolved in a mixture of CCl_4 (20 ml) and petroleum ether b.p. 40—60° C (10 ml). Careful bubbling of Cl_2 gas through this solution caused precipitation of compound **5d** as a yellow solid, 0.86 g, 39% yield, m.p. 229—230°C (acetonitrile). IR (KBr): 3120w, 1590m, 1570w, 1530m, 1250m, 1200w, 1100m, 1025m, 930m, 840s, 730m, 710m cm^{-1}.

3-Choro-6-methylbenzo[b]tellurophene (4d). An ether suspension of the dichloride **5d** was shaken thoroughly with $Na_2S_2O_5$ (5% aq.) until all material had dissolved. Drying ($CaCl_2$) and evaporation of the organic phase yielded compound **4d** as a yellow crystalline solid, m.p. 49—50° C (petroleum ether b.p. 40—60° C) in almost quantitative yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 2.41 (3H, s), 7.26 (1H, d, J = 7.9 Hz), 7.72 (1H, s), 7.80 (1H, d, J = 8.0 Hz), 8.29 ppm (1H, s). Mass spectrum: *m/e* (rel. intensity, *m/e* > 100, only peaks stronger than 10% of the base peak) 282(24), 281(13), 280(95), 279(20), 278(83), 277(24), 276(47), 275(23), 274(10), 245(17), 243(17), 241(11), 151(10), 150(17), 149(24), 116(19), 115(100), 114(34), 113(20). IR (KBr): 3080w, 2910w, 1590m, 1445m, 1280m, 1250m, 1105w, 1030m, 920m, 910m, 810s, 750s, 690m, 660m cm^{-1}.

6-Bromo-3-chlorobenzo[b]tellurophene 1,1-dichloride (5e). 4-Bromophenylacetylene (1.6 g, 8.9 mmol), TeO_2 (0.5 g, 3.2 mmol) and LiCl (0.9 g, 21.2 mmol) were refluxed in acetic acid (50 ml) for 48 h. Filtration and cooling separated 0.15 g, 9% yield of compound **6c** m.p. 238—240° C (acetonitrile). Mass spectrum: *m/e* (rel. intensity, *m/e* ⩾ 100, only peaks stronger than 10% of the base peak) 562(39), 560(58), 558(54), 556(30), 526(14), 524(26), 522(26), 520(17), 490(17), 488(12), 446(23), 444(33), 442(26), 440(12), 318(29), 316(45), 314(24), 280(15), 278(11), 237(17), 222(18), 200(73), 199(29), 198(20), 182(100), 180(100), 101(85), 100(30). IR (KBr): 3030w, 1585m, 1570m, 1550m, 1485s, 1390m, 1070s, 1005m, 930w, 900s, 830s, 810m,

750m, 650w cm^{-1}. The acetic acid solution was poured into ethyl ether (150 ml) and neutralized with $NaHCO_3$ (5% aq.). Drying ($CaCl_2$) and evaporation of the organic phase yielded a brown oil which was dissolved in a mixture of CCl_4 (20 ml) and petroleum ether b.p. 40—60°C (10 ml). Careful bubbling of Cl_2 gas through this solution caused precipitation of compound 5e as a yellow solid, 1.0 g, 77% yield. M.p. 280—281°C (acetonitrile). IR (KBr): 3070w, 1560m, 1525m, 1440w, 1370w, 1250m, 1100w, 1080w, 1060w, 920s, 840m, 745m, 730w cm^{-1}.

6-Bromo-3-chlorobenzo[b]tellurophene (4e). An ether suspension of the dichloride 5e was shaken thoroughly with $Na_2S_2O_5$ (5% aq.) until all material had dissolved. Drying ($CaCl_2$) and evaporation of the organic phase yielded compound 4e as a yellow solid in almost quantitative yield. M.p. 97—98°C (acetonitrile). ^1H NMR ($CDCl_3$, Me_4Si) δ 7.57 (1H, dd, J = 1.7 Hz and J = 8.5 Hz), 7.77 (1H, d, J = 8.5 Hz), 8.06 (1H, d, J = 1.7 Hz), 8.42 ppm (1H, s). Mass spectrum: *m/e* (rel. intensity, $m/e \geq 100$, only peaks stronger than 10% of the base peak) 348(15), 346(68), 344(100), 342(72), 340(34), 265(10), 230(10), 228(10), 216(26), 214(21), 135(11), 130(10), 128(10), 100(34). IR (KBr): 3080w, 1670m, 1645m, 1435m, 1280w, 1240w, 1075w, 915m, 850m, 805s, 760m, 680w, 660w cm^{-1}.

3-Bromo-2-methylbenzo[b]tellurophene 1,1-dichloride (12a). 1-Phenyl-1-propyne (2.0 g, 17.2 mmol), TeO_2 (1.0 g, 6.3 mmol) and LiBr (2.0 g, 23.0 mmol) were refluxed in acetic acid (50 ml) for 20 h, cooled to room temperature and poured into ethyl ether (150 ml) and neutralized with $NaHCO_3$ (5% aq.). Drying ($CaCl_2$) and evaporation of the organic phase yielded a brown oil which was dissolved in a mixture of CCl_4 (20 ml) and petroleum ether b.p. 40—60°C (10 ml). Careful bubbling of Cl_2 gas through this solution caused precipitation of compound 12a as a yellow solid, 1.2 g, 49% yield. M.p. 249—251°C (acetonitrile). Mass spectrum: *m/e* (rel. intensity, $m/e > 100$, only peaks stronger than 10% of the base peak) 326(14), 324(27), 322(19), 320(10), 245(12), 243(11), 186(12), 149(10), 115(100). IR (KBr): 1590m, 1445w, 1435m, 1425w, 1230m, 1160w, 995m, 900m, 870m, 840s, 710w, 640w cm^{-1}.

3-Bromo-2-methylbenzo[b]tellurophene (11a). An ether suspension of the dichloride 12a was shaken thoroughly with $Na_2S_2O_5$ (5% aq.) until all material had dissolved. Drying ($CaCl_2$) and evaporation of the organic phase yielded compound 11a as an oil in almost quantitative yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 2.60 (3H, s), 7.16 (1H, t, J = 7.7 Hz), 7.41 (1H, t, J = 7.8 Hz), 7.79 (1H, d, J = 7.8 Hz), 7.89 (1H, d, J = 8.6 Hz) ppm. IR (neat): 3050w, 2950w, 2840w, 1445m, 1430m, 1240m, 1020m, 900m, 850s, 710m, 670w, 650m cm^{-1}.

3-Chloro-2-methylbenzo[b]tellurophene 1,1-dichloride (12b). 1-Phenyl-1-propyne (1.05 g, 9.0 mmol), TeO_2 (0.5 g, 3.1 mmol) and LiCl (1.0 g, 23.5 mmol) were refluxed in acetic acid (40 ml) for 48 h, cooled to room temperature and poured into ethyl ether (150 ml) and neutralized with $NaHCO_3$ (5% aq.). Drying ($CaCl_2$) of the organic phase and evaporation yielded a brown oil which was dissolved in a mixture of CCl_4 (10 ml) and petroleum ether b.p. 40—60°C (5 ml). Careful bubbling of Cl_2 gas through this solution caused precipitation of compound 12b as a yellow solid, 0.30 g, 28% yield. M.p. 268—270°C (acetonitrile). Mass spectrum: *m/e* (rel. intensity, only peaks stronger than 5% of the base peak above m/e = 100) 282(10), 280(38), 278(33), 276(18),

275(8), 274(6), 245(11), 243(10), 241(7), 152(7), 151(8), 150(21), 149(16), 116(10), 115(100), 114(16), 113(10). IR (KBr): 1590m, 1445w, 1435m, 1240m, 1235w, 1160w, 1020w, 1000m, 925m, 920m, 770m, 760s, 715w cm^{-1}.

3-Chloro-2-methylbenzo[b]tellurophene (11b). An ether suspension of the dichloride 12b was shaken thoroughly with $Na_2S_2O_5$ (5% aq.) until all material had dissolved. Drying ($CaCl_2$) and evaporation of the organic phase yielded compound 11b as an oil in almost quantitative yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 2.60 (3H, s), 7.17 (1H, t, J = 7.6 Hz), 7.41 (1H, t, J = 7.6 Hz), 7.78 (1H, d, J = 7.3 Hz), 7.82 ppm (1H, d, J = 8.3 Hz) IR (neat): 3040w, 2910w, 2840w, 1565w, 1450m, 1430s, 1245m, 1020m, 755s, 715m, 700(m), 660w cm^{-1}.

3-Oxo-2,3-dihydrobenzo[b]tellurophene (3) from compound 4a. 3-Chlorobenzo[*b*]tellurophene (0.18 g, 0.68 mmol) was refluxed in trifluoroacetic acid (25 ml) for 2.5 h, poured into ethyl ether (100 ml) and water (100 ml) and neutralized with Na_2CO_3. The two-phase system was left overnight and the organic phase was dried ($CaCl_2$) and evaporated to give 0.14 g, 83% yield of compound 3, m.p. 107° C (cyclohexane, lit, 107° C [3]). The compound was identical with an original sample generously provided by Prof. Klaus Praefcke, Institut für Organische Chemie der Technischen Universität Berlin [23].

Butyl-2-ethynylphenyltelluride (13). Butyl lithium (1.95 mmol, 20% excess) in hexane was added to a solution of 3-bromobenzo[*b*]tellurophene (0.5 g, 1.62 mmol) in dry ether (30 ml) cooled to —50° C. After 30 min the reaction mixture was hydrolyzed with wet ether and water and the organic phase separated, dried ($CaCl_2$) and evaporated. The resulting oil was chromatographed on silica gel (R_f = 0.5, petroleum ether b.p. 40—60° C) to yield 0.33 g, 71% yield, of compound 13. The same reaction product was obtained when the reaction was performed at —100°C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.92 (3H, t), 1.39 (2H, m), 1.83 (2H, m), 2.95 (2H, t), 3.39 (1H, s), 7.15—7.54 ppm (4H, several peaks). IR (neat): 3290s, 3050w, 2950m, 2920m, 2100w, 1580w, 1450m, 1435w, 1425w, 1250w, 1160w, 1045w, 1020m, 750s cm^{-1}.

3-Ethoxy-2-ethynylphenylbenzo[b]tellurophene (14). Compound 6 (0.09 g, 0.22 mmol) was dissolved in a sodium ethoxide solution (prepared from sodium, 0.03 g, and ethanol, 25 ml) and refluxed for 5 h. The cooled solution was poured into ethyl ether (100 ml) and shaken with water (2 × 100 ml). The organic phase was dried ($CaCl_2$) and evaporated to yield a yellow oil which was purified on a preparative SiO_2 TLC-plate (petroleum ether b.p. 40—60° C, R_f = 0.4). 0.05 g, 59% yield of compound 14 was isolated. ^1H NMR ($CDCl_3$, Me_4Si) δ 1.50 (3H, t), 4.75 (2H, q), 7.25—7.80 ppm (9H, several peaks). Mass spectrum: *m/e* (rel. intensity, *m/e* > 100, only peaks stronger than 10% of the base peak) 376(28), 374(24), 372(17), 349(30), 347(28), 345(19), 248(44), 220(11), 217(15), 181(30), 180(13), 179(66), 177(12), 149(15), 115(20), 113(17), 105(100). IR (neat): 3050w, 2970w, 2920w, 2180m, 1600w, 1560m, 1530m, 1485m, 1450m, 1370w, 1310s, 1160m, 1030s, 900m, 750s, 720m, 690m cm^{-1}.

Attempted cyclization of 2-chloro-2-phenylvinyltellurium trichloride in HOAc. 2-Chloro-2-phenylvinyltellurium trichloride (1.5 g, 4.0 mmol) was refluxed in HOAc (30 ml) for 36 h, cooled to room temperature and poured into ethyl ether (100 ml) and neutralized with $NaHCO_3$ (5% aq.). The organic

phase was dried ($CaCl_2$) and evaporated to yield an oil which was filtered through a short SiO_2 column (CH_2Cl_2/petroleum ether b.p. 40—60°C 1 : 1) giving 0.6 g, 74% yield, of bis(2-chloro-2-phenylvinyl)telluride (18) m.p. 59—60°C (lit. 59—61°C [5]). NMR-analysis of the crude reaction product revealed no formation of 3-chlorobenzo[*b*]tellurophene.

Attempted cyclization of 2-chloro-2-phenylvinyltellurium trichloride in HOAc/LiCl. 2-Chloro-2-phenylvinyltellurium trichloride (1.5 g, 4.0 mmol) and LiCl (2.0 g, 47.2 mmol) were refluxed in acetic acid (35 ml) for 24 h, cooled to room temperature and poured into ethyl ether (100 ml) and neutralized with $NaHCO_3$ (5% aq.). The organic phase was dried ($CaCl_2$) and evaporated to yield an oil which was filtered through a short SiO_2-column (CH_2Cl_2/petroleum ether b.p. 40—60°C 1 : 1) giving a mixture of 3-chlorobenzo[*b*]tellurophene (0.4 g, 38% yield) and bis(2-chloro-2-phenylvinyl)telluride (18) (0.2 g, 25% yield) as revealed by ^1H NMR spectroscopy and GLC analysis.

Acknowledgement

Prof. Klaus Praefcke, Institut für Organische Chemie der Technischen Universität Berlin is gratefully acknowledged for a generous gift of 3-oxo-2,3-dihydrobenzo[*b*]tellurophene.

Financial support by the Swedish Natural Science Research Council and Carl Tryggers Stiftelse is gratefully acknowledged.

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