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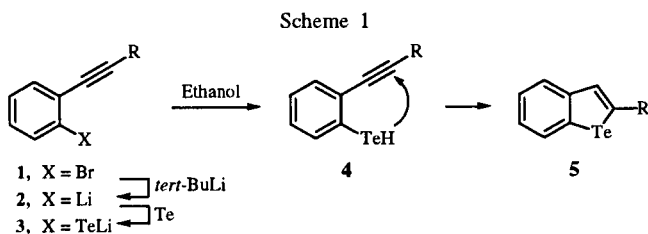
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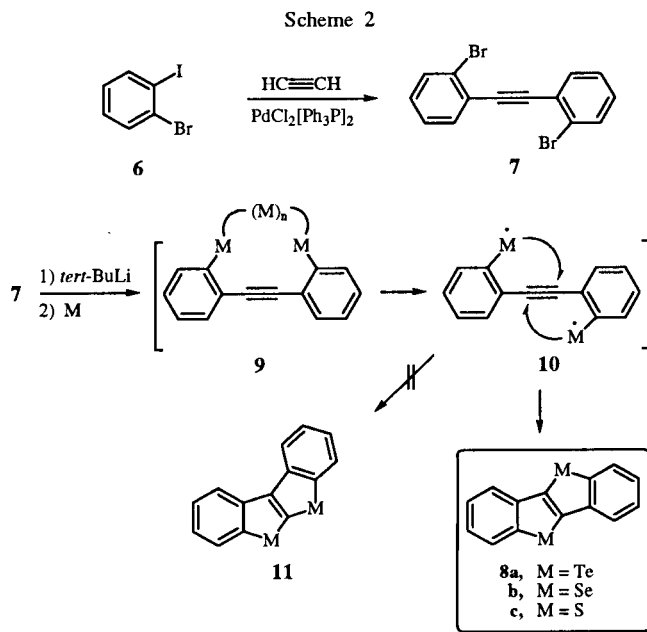
Treatment of 2, 2'-dibromodiphenylacetylene **7** with *tert*-butyllithium followed by tellurium insertion resulted in intramolecular ring closure to afford [1]benzotelluro[3,2-*b*][1]benzotellurophene **8a**. Similarly, [1]benzoseleno[3,2-*b*][1]benzoselenophene **8b** and [1]benzothieno[3,2-*b*][1]benzothiophene **8c** were also obtained.

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The chemistry of benzo[*b*]thiophenes [2], benzo[*b*]selenophenes [3], and benzo[*b*]tellurophenes [4] have been reviewed and are solid and well-done. Various synthetic methods for the preparation of these compounds have been provided up to now. We have previously described the synthesis of various heterocycles [5] containing a chalcogen element (Te, Se, and S) by the intramolecular ring closure of a chalcogenol to an ethynyl group, moreover, reported a convenient versatile one-pot preparation of benzo[*b*]tellurophenes **5** [6] via the phenyltellurols **4** and their selenium and sulfur analogues from *o*-bromoethynyl benzenes **1** (Scheme 1). This paper describes the extension of our synthetic methodology for the preparation of the title compounds; [1]benzoseleno[3,2-*b*][1]benzoselenophene **8b** [7] was already prepared by the acid-induced condensation of *o*-methylselenobenzaldehyde, and [1]benzothieno[3,2-*b*][1]benzothiophene **8c** [8] was also obtained by the reaction of thiosalicylic acid with phosphorus pentoxide. However, its tellurium analogues **8a** was hitherto unknown.



The synthesis of **8** is shown in Scheme 2. The key starting compound, 2,2'-dibromodiphenyl acetylene **7** were easily prepared by palladium-catalyzed coupling reaction of *o*-bromoiodobenzene **6** [6] with acetylene according to Sonogashira's method [9] in 77% yield. The acetylenic compound **7** was lithiated with *tert*-butyllithium in anhydrous tetrahydrofuran at -80° , and then treated with tellurium powder, giving [1]benzotelluro[3,2-*b*][1]benzotellurophene **8a** in 55% yield, together with diphenylacetylene in *ca.* 10% yield. The mass spectrum of this compound showed a molecular formula of $\text{C}_{14}\text{H}_8\text{Te}_2$ with a molecular ion at $m/z = 436$ (^{130}Te) having the isotope pattern of Te_2 . The ^1H -nmr spec-



trum had two double-doublets signals at 7.16 and 7.44, and two doublets signals at 7.66 and 7.96, respectively. The ^{13}C -nmr spectrum showed three singlet sp^2 carbons at 129.6, 130.9, and 147.6. These spectral data clearly indicate that the structure of the product is **8a**; the ^{13}C -nmr spectrum of **11** should have four singlet sp^2 carbons. [1]Benzoseleno[3,2-*b*][1]benzoselenophene **8b** and [1]benzothieno[3,2-*b*][1]benzothiophene **8c** were prepared in an analogous manner using selenium or sulfur instead of tellurium. No structural isomer, **11** was obtained. In order to prepare benzo[*b*]tellurophenes **5** [6] from *o*-bromoethynylbenzenes **1**, addition of a proton source such as ethanol after tellurium element insertion was essential (Scheme 1), but in the present case, addition of proton source was not indispensable. Thus, this tandem ring closure reaction yielding **8** may probably proceed via a radical mechanism through intermediates **9** and **10**. Spectral data for the known compounds **8b** and **8c** were not given in the literature [7,8], so they are also reported here. These results and spectral data are summarized in the Table.

Table

[1]Benzotelluro[3,2-*b*][1]benzotellurophene **8a**, [1]Benzoseleno[3,2-*b*][1]benzoselenophene **8b**, and [1]benzothieno[3,2-*b*][1]benzothiophene **8c**

Compound No.	Yield (%)	Appearance mp	Formula HRMS Calcd. (Found)	¹ H-NMR (400 MHz) J = Hz	¹³ C-NMR (100 MHz)
8a M = Te	55	yellow prisms mp 232-234°	C ₁₄ H ₈ Te ₂ 435.8751 (435.8719)	7.16 (2H, dd, J = 7.3, 7.7) 7.40 (2H, dd, J = 7.3, 7.7) 7.66 (2H, d, J = 7.7) 7.96 (2H, d, J = 7.3)	125.0 (d), 126.3 (d), 127.3 (d), 129.6 (s), 130.9 (s), 132.7 (d), 147.6 (s)
8b M = Se	52	colorless prisms mp 207-208° (Lit. [7] mp 208-209°)	C ₁₄ H ₈ Se ₂ 335.8956 (335.8932)	7.30 (2H, dd, J = 7.0, 8.4) 7.43 (2H, dd, J = 7.0, 8.1) 7.78 (2H, d, J = 8.4) 7.94 (2H, d, J = 8.1)	123.8 (d), 125.1 (d), 125.4 (d), 126.8 (d), 134.3 (s), 137.8 (s), 141.3 (s)
8c M = S	49	colorless prisms mp 217-218° (Lit. [8] mp 214-216°)	C ₁₄ H ₈ S ₂ 240.0067 (240.0061)	7.40 (2H, dd, J = 7.3, 7.7) 7.43 (2H, dd, J = 7.3, 7.7) 7.78 (2H, d, J = 7.3) 7.94 (2H, d, J = 7.7)	121.6 (d), 124.0 (d), 124.9 (d), 125.0 (d), 133.1 (s), 134.1 (s), 142.2 (s)

EXPERIMENTAL

General Methods.

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. Mass spectra and high resolution mass were recorded on a JEOL JMS-DX300 instrument. The ¹H nmr spectra and the ¹³C nmr spectra were determined with a JEOL PMX-60SI (60 MHz), JEOL EX-90A (90 MHz) or JEOL JNMGSX 400 (400 MHz) spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. Microanalyses were performed in the Microanalytical Laboratory of this Faculty.

Synthesis of 2,2'-Dibromodiphenylacetylene **7**.

Cuprous iodide (160 mg) and bis(triphenylphosphine)palladium dichloride (280 mg) were added to a mixture of *o*-bromiodobenzene (**6**, 14.2 g, 50 mmol) in benzene (100 ml) and piperidine (80 ml). A slow current of acetylene was passed through the reaction mixture at 80° with stirring until disappearance of the starting material (about 3 hours). After cooling, cold water was added to the mixture, and the resulting aqueous mixture was extracted with benzene (100 ml x 3). The combined organic extract was washed with water (200 ml x 3), 5% sulfuric acid (200 ml x 3), saturated aqueous sodium hydrogen carbonate (200 ml x 2) and brine (200 ml x 2), then dried over magnesium sulfate. Benzene was removed *in vacuo*. The residue was chromatographed on silica gel using *n*-hexane:methylene chloride (10:1, v/v) as an eluent to give **7**, which was recrystallized from acetone-*n*-hexane to give 6.49 g of **7** (colorless prisms, mp 81-83°) in 77% yield; ms: m/z 334, 336, 338 (M⁺).

Anal. Calcd. for C₁₄H₈Br₂: C, 50.04; H, 2.40. Found: C, 50.31; H, 2.55.

Preparation of [1]Benzotelluro[3,2-*b*][1]benzotellurophene **8a**.

To a stirring solution of 2,2'-dibromodiphenylacetylene (**1**, 1.69 g, 5 mmol) in anhydrous tetrahydrofuran (50 ml) at -80° under an argon atmosphere was slowly added *tert*-butyllithium (1.5 moles in pentane solution, 10 ml, 15 mmol). The reaction mixture was stirred at the same temperature for 30 minutes. Powdered tellurium (1.92 g, 15 mmol) was added to the reaction mixture all at one portion, then the cooling bath was removed and the mixture was

allowed to rise to room temperature during 3-4 hours. The resulting mixture was further stirred for 3 hours under the conditions, poured into ice-water, and then extracted with ethyl acetate (100 ml x 3). The organic extract was washed with brine (100 ml x 2), dried over magnesium sulfate, and concentrated *in vacuo*. The residue was purified by silica gel chromatography using *n*-hexane:methylene chloride (10:1, v/v) as an eluent to give **8a**.

Anal. Calcd. for C₁₄H₈Te₂: C, 38.98; H, 1.87. Found: C, 38.90; H, 1.99.

Preparation of [1]Benzoseleno[3,2-*b*][1]benzoselenophene **8b**.

The acetylene **7** was treated with selenium powder instead of tellurium and worked up as described for the preparation of **8a** to give **8b**.

Preparation of [1]Benzothiolo[3,2-*b*][1]benzothiophene **8c**.

The acetylene **7** was treated with sulfur powder instead of tellurium and worked up as described for the preparation of **8a** to give **8c**.

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