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Advanced Synthesis & Catalysis

One-Pot Synthesis of 3-Halo-2-organochalcogenylbenzo[*b*]chalcogenophenes from 1-(2,2-Dibromovinyl)-2-organochalcogenylbenzenes

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Abstract: A transition-metal-free one-pot synthesis of 3-halo-2-organochalcogenylbenzo[*b*]chalcogenophenes has been developed using 1-(2-organochalcogenylethynyl)-2-butylchalcogenylbenzenes generated *in situ* from 1-(2,2-dibromovinyl)-2-organochalcogenylbenzenes and diorganoyl dichalcogenides. By this method, several 2,3-disubstituted benzo[*b*]chalcogenophenes were prepared in yields of 48–93%. The mechanistic investigation suggests that the formation of chalcogenoacetylenes containing an adjacent chalcogen atom in the first step of this one-pot procedure involves acetylide anions formed from 1-(2,2-dibromovinyl)-2-organochalcogenylbenzenes and mild bases.

Keywords: chalcogenoacetylenes; benzo[*b*]chalcogenophenes; one-pot; 1-(2,2-dibromovinyl)-2-organochalcogenylbenzenes

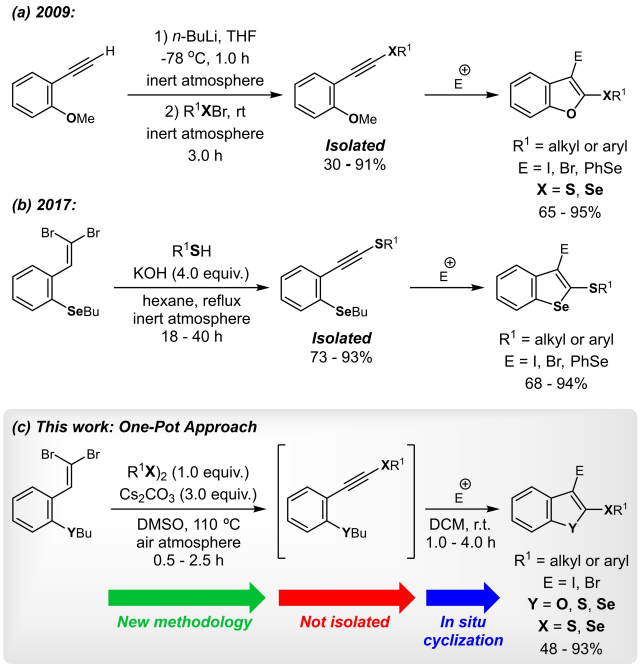
Introduction

Chalcogenophene derivatives are important structural ring systems in materials science,[1] medicinal chemistry,[2] electrochemistry,[3] agrochemistry,[2a,4] and organic synthesis.[5] In particular, the π-extended benzo[*b*]chalcogenophene derivatives have attracted great attention due to their improved properties as materials for optoelectronic devices such as organic field-effect transistors (OFETs),[6] organic photovoltaics (OPVs),[7] organic light-emitting diodes (OLEDs),[8] liquid-crystal displays (LCDs),[9] and optical sensors.[10] In addition, these organic frameworks show diverse potential applications in drug discovery, and nowadays several of these chalcogen-heterocycles are available on the market.[2] Therefore, the straightforward synthesis of this class of compounds is of great interest in chemistry.

There is a variety of synthetic methodologies for synthesis of benzo[*b*]chalcogenophenes, including electrophile-promoted nucleophilic cyclizations,[11] intramolecular nucleophilic additions[12] and radical cyclizations,[13] intramolecular condensations,[14] transition-metal-catalyzed reactions,[15] and hypervalent iodine-mediated cyclizations.[16] Despite these advances, current methods usually employ a number of separated steps which are both time- and cost-consuming. This is especially important when the degree of substitution of the heteroarene is high, as in 2,3-disubstituted benzo[*b*]chalcogenophenes.

In this regard, chalcogenoacetylenes are very useful intermediates (Scheme 1), since through electrophile-promoted nucleophilic cyclization of an adjacent chalcogen atom several 3-halo-2-organochalcogenylbenzo[*b*]chalcogenophenes can be prepared and further functionalized by cross-coupling reactions for the synthesis of more complex molecules.[11,17]

However, the preparation of these key chalcogenoacetylene intermediates requires purification steps or harsh reaction conditions before cyclization



Scheme 1. Synthesis of 3-halo-2-organochalcogenylbenzo[*b*] chalcogenophenes.

(Scheme 1a).[17] On the other hand, 1,1-dibromoalkenes containing an adjacent heteroatom have emerged as an interesting possibility, along with thiols in basic media for the synthesis of chalcogenoacetylenes;[17b] however, there are still purification steps involved, and the handling of thiols is not easy.

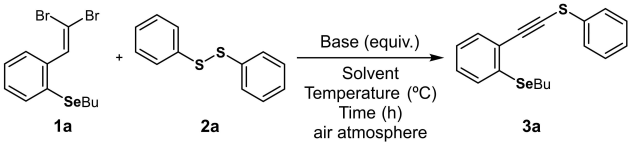
Inspired by these pioneering works, we observed that the easily handled diorganoyl disulfides could be alternative and complementary reagents for the synthesis of 3-halo-2-organochalcogenylbenzo[*b*] chalcogenophenes from 1-(2,2-dibromovinyl)-2-organochalcogenylbenzenes using a sequential one-pot metal-free two-step procedure (Scheme 1c). The mechanism of 1-(2-organochalcogenylethynyl)-2-butylchalcogenylbenzenes formation in the first step puzzled us, since ordinarily it requires a nucleophilic organosulfur or organoselenium species,[17b,18] and yet only cesium carbonate was employed along with the diorganoyl dichalcogenide. Therefore, a mechanistic investigation of this reaction is indispensable. Additionally, the key 1-(2-organochalcogenylethynyl)-2-butylchalcogenylbenzenes intermediate could be converted in high yield to the expected products in the same pot without isolation, which is a noteworthy finding in the synthesis of this class of relevant compounds.

As part of our continuous endeavor to develop efficient methods for the construction of organochalcogen compounds,[19] herein we describe the first one-pot synthesis of 3-halo-2-organochalcogenylbenzo[*b*] chalcogenophenes from the appropriate 1-(2,2-dibromovinyl)-2-organochalcogenylbenzenes (Scheme 1c). We also carried out several control experiments in order to gain insights into the reaction mechanism in the first chalcogenoacetylene formation step.

Results and Discussion

Initial optimization efforts were focused on the formation of the key intermediate 1-(2-phenylsulfanylethynyl)-2-butylselenanylbenzene (**3 a**) from **1 a** and diphenyl disulfide (**2 a**; Table 1). Interestingly, we observed that **3 a** was produced in 19% yield when only *t*-BuOLi was employed, which in fact typifies a new transition-metal-free methodology for the synthesis of thioacetylenes (Table 1, entry 1) from 1,1-dibromoalkenes and diorganoyl disulfides. Under these conditions, the terminal alkyne butyl(2-ethynylphenyl)

Table 1. Optimization studies for the synthesis of **3 a**.



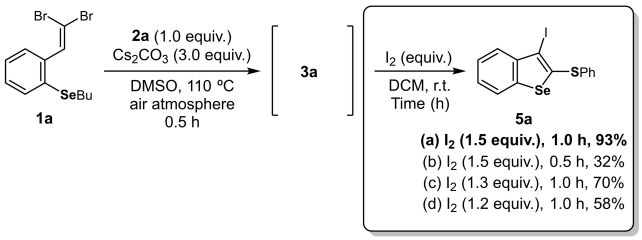
#[a]	Base (equiv.)	Solvent	Temp. [°C]	t. [h]	3a [%][b]
1	*t*-BuOLi (4)	DMSO	110	12	19[c]
2	*t*-BuOLi (3)	DMSO	110	12	83[c]
3	*t*-BuONa (3)	DMSO	110	12	58[c]
4	*t*-BuOK (3)	DMSO	110	12	45[c]
5	K_3PO_4 (3)	DMSO	110	12	70[c]
6	Na_2CO_3 (3)	DMSO	110	12	15
7	K_2CO_3 (3)	DMSO	110	12	63
8	Cs_2CO_3 (3)	DMSO	110	12	89
9	Cs_2CO_3 (2)	DMSO	110	12	51
10	Cs_2CO_3 (3)	DMSO	120	12	65[c]
11	Cs_2CO_3 (3)	DMSO	140	12	42[c]
12	Cs_2CO_3 (3)	DMSO	100	12	26
13	Cs_2CO_3 (3)	DMSO	110	1.0	93
14	Cs_2CO_3 (3)	DMSO	110	0.5	95
15	Cs_2CO_3 (3)	DMSO	110	0.25	70
16	Cs_2CO_3 (3)	DMF	110	0.5	14
17	Cs_2CO_3 (3)	NMP	110	0.5	5
18	Cs_2CO_3 (3)	Toluene	110	0.5	–
19	Cs_2CO_3 (3)	EtOH	110	0.5	–
20	Cs_2CO_3 (3)	DMSO	110	0.5	47[d]
21	Cs_2CO_3 (3)	DMSO	110	0.5	64[e]
22	Cs_2CO_3 (3)	DMSO	110	0.5	42[f]

[a] Reaction conditions: **1 a** (1.0 equiv., 0.28 mmol), **2 a** (1.0 equiv., 0.14 mmol), base (equiv.), DMSO (2.0 mL), air atmosphere.
[b] Isolated yields.
[c] The terminal alkyne butyl(2-ethynylphenyl)selane (**4 a**) was detected by GC-MS as side product in the experiment.
[d] Under argon atmosphere.
[e] Under O_2 atmosphere.
[f] **2 a** (0.5 equiv., 0.07 mmol).

selane (**4a**) was observed as side product along with the starting materials **1a** and **2a**.[20] In fact, the product **3a** was obtained in 83% yield by performing the reaction with 3.0 equivalents of base (Table 1, entry 2), but other *tert*-butoxides did not improve the yield further (Table 1, entries 3 and 4). Additionally, in the presence of a weaker base such as K_3PO_4 the yield of **3a** was 70% (Table 1, entry 5), and only traces of **4a** were detected by GC-MS analysis of the crude reaction mixture.

On the other hand, we found that 3.0 equivalents of K_2CO_3 completely suppressed the formation of the side product **4a**, but the expected **3a** was obtained in only moderate yield (Table 1, entry 7). The use of Na_2CO_3 furnished **3a** in low yield, also with no side products (Table 1, entry 6); however, under the same reaction conditions the base Cs_2CO_3 cleanly provided 89% yield of **3a** (Table 1, entry 8). Further optimization revealed that lower amounts of Cs_2CO_3 (Table 1, entry 9) or temperatures either higher or lower than 110 °C resulted in substantial reductions in the yield of **3a** (Table 1, entries 10–12). Fortunately, the reaction yield remained high, even after only 0.5 h (Table 1, entries 13 and 14), but shorter time gave the product **3a** in 70% yield (Table 1, entry 15). Other solvents, such as DMF (*N,N*-dimethylformamide) and NMP (*N*-Methyl-2-pyrrolidone), led to lower yields (Table 1, entries 16 and 17), and the reaction did not occur at all in toluene or ethanol (Table 1, entries 18 and 19). When the reaction was carried out under an argon atmosphere, only 47% of the product **3a** was obtained, which indicates that an oxidizing medium is necessary for the reaction (Table 1, entry 20). Although, when the reaction was developed under molecular oxygen atmosphere the yield of **3a** was 64%, which indicates that an excess of O_2 was not beneficial to the reaction yield (Table 1, entry 21). Additionally, when the reaction was developed with 0.5 equiv. of **2a**, only 42% yield of **3a** was obtained (Table 1, entry 22).

Considering the excellent yield of **3a** achieved in a short reaction time under simple reaction conditions (Table 1, entry 14), we envisioned that the molecular complexity could be further increased through an one-pot electrophile-promoted intramolecular nucleophilic cyclization by the simple addition of I_2 as electrophile (Scheme 2). In this way, after an experiment under the optimized reaction conditions (Table 1, entry 14), the system was cooled to room temperature and a solution of 1.5 equivalents of I_2 in dichloromethane was added to the system.[11,17] The progress of the second step of this one-pot process was monitored by thin-layer chromatography (TLC), which indicated the total conversion of **3a** after only 1.0 h, thereby providing 93% yield of the expected product **5a** (Scheme 2a). After rapid screening of the second-step conditions, we observed that shorter reaction times (Scheme 2b) or



Scheme 2. One-pot two step synthesis fo **5a**.

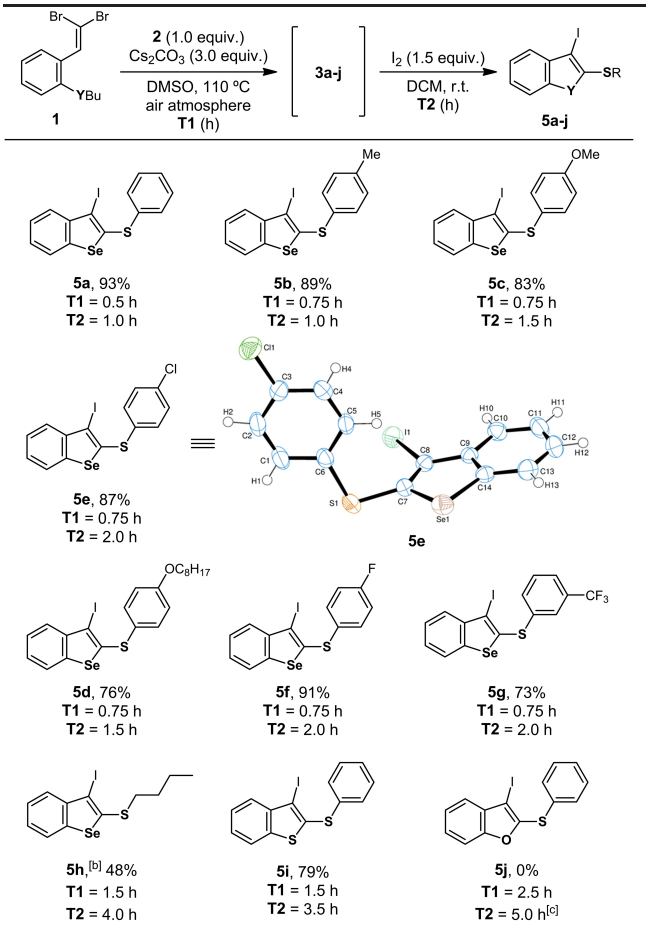
lower amounts of I_2 (Scheme 2c and 2d) decreased the yield of **5a**.

Once the optimum conditions for both steps were found, we explored further the scope and limitations of the one-pot synthesis of 3-halo-2-organochalcogenyl-benzo[*b*]chalcogenophenes using several diorganoyl dichalcogenides (**2** and **6**) and 1-(2,2-dibromovinyl)-2-organochalcogenylbenzenes (**1a**, **1b** and **1c**; Tables 2–4). The reaction times of the first and second steps (**T1** and **T2**) were monitored by TLC. In general, the first step required a short reaction time when diaryl disulfides were employed (**2a–g**; Table 2), and no clear electronic effects were encountered from substituents on the *S*-aryl group. A slight longer **T1** time was observed only when the phenyl rings on the diaryl disulfides were substituted with either electron-donating or electron-withdrawing groups, although the reaction with dibutyl disulfide (**2h**) clearly took longer **T1** and **T2** times to afford a moderate yield of **5h**. The **T2** times were also longer in the *in situ* I_2-promoted nucleophilic cyclizations of **3c–g**; that is, when its *S*-aryl groups were substituted with electron-donating or electron-withdrawing groups, good to excellent yields of **5c–g** were obtained. On the other hand, the compounds **5a** and **5b** were achieved in 93% and 89% yields, respectively, after a **T1** time of 1.0 h.

Structural characterization of the 3-halo-2-chalcogenylbenzo[*b*]chalcogenophenes was based on NMR analysis and confirmed by single-crystal X-ray diffraction of **5e** (Table 2), which proved the *5-endo-dig* cyclization in the second step of the one-pot process.[21] Further diversity in the general structure **5** was introduced by the use of 1-(2,2-dibromovinyl)-2-butylthiobenzene (**1b**), which after longer **T1** and **T2** reaction times afforded **5i** in 79% yield. Despite the efficient production of the intermediate **3j** after a **T1** time of 2.5 h (observed by GC-MS analysis), the product **5j** was not detected even after a longer time at higher temperature in the second step. These results indicated that the lower nucleophilicity of oxygen[11k] added to the steric hindrance from the butyl chain[11k,17a] significantly suppressed the second step of the one-pot reaction.

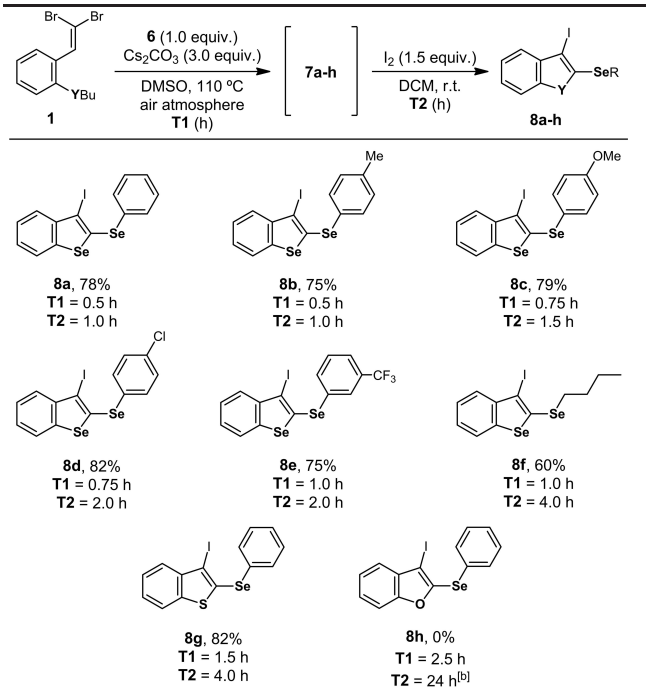
The reaction also preceded efficiently with diversely substituted diorganoyl diselenides (**6a–g**)

Table 2. Scope of the one-pot procedure to prepare the compounds **5a–j**.



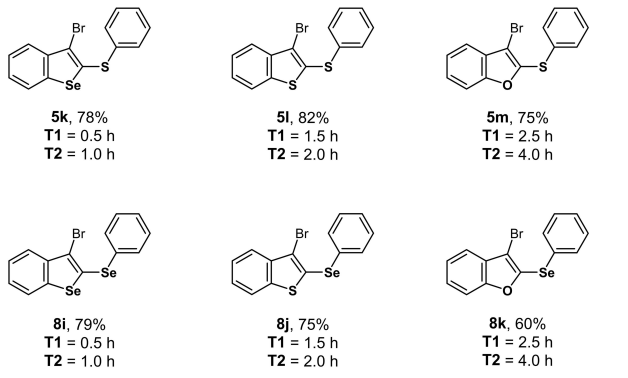
[a] Reaction conditions: **1** (0.25 mmol, 1.0 equiv.), (0.125 mmol, 1.0 equiv.), Cs_2CO_3 (0.75 mmol, 3.0 equiv.), DMSO (2.0 mL), air atmohphere, I_2 (1.5 equiv., 0.37 mmol), DCM (2.0 mL).
[b] 1.0 equiv. of **2h**.
[c] 45 °C at second step.

Table 3. Scope of the one-pot procedure to prepare the compounds **8a–h**.



[a] Reaction conditions: **1** (0.25 mmol, 1.0 equiv.), **6** (0.125 mmol, 1.0 equiv.), Cs_2CO_3 (0.75 mmol, 3.0 equiv.), DMSO (2.0 mL), air atmosphere, I_2 (1.5 equiv., 0.37 mmol), DCM (2.0 mL).
[b] 45 °C at second step.

Table 4. NBS as electrophilic source in the second step of the one-pot procedure (**5k–m**, **8i–k**).



[a] Reaction conditions: **1a–c** (0.25 mmol, 1.0 equiv.), **2a** or **6a** (0.125 mmol, 1.0 equiv.), Cs_2CO_3 (0.75 mmol, 3.0 equiv.), DMSO (2.0 mL), air atmosphere, NBS (2.5 equiv., 0.62 mmol), DCM (2.0 mL).
[b] 45 °C at second step.

(Table 3). In general, the yields of the corresponding 3-iodo-2-organoselenylbenzo[*b*]chalcogenophenes (**8a–g**) were slightly lower than for **5a–i**, and similar times of reactions were reported. The **T1** time was also shorter with diaryl diselenides (**6a–e**), and again no clear electronic effects were observed from substituents on the *Se*-aryl group. The **T1** time was longer with dibutyl diselenide (**6f**), as well the **T2** time in the second step with the *in situ*-produced **7f**. The observed **T2** times of reactions were also longer when the *Se*-aryl groups on **7a–e** were substituted with electron-donating or electron-withdrawing groups. The one-pot procedure for the synthesis of benzo[*b*]thiophenes also took longer **T1** and **T2** times, and the compound **8g** was obtained in good yield. The compound **8h** could not be produced by this one-pot reaction from **1c**, but the intermediate **7h** was produced efficiently after 2.5 h of the first step of the one-pot procedure, as detected by GC-MS analysis.

The use of NBS in the second step of this one-pot procedure was also investigated with the 1-(2,2-

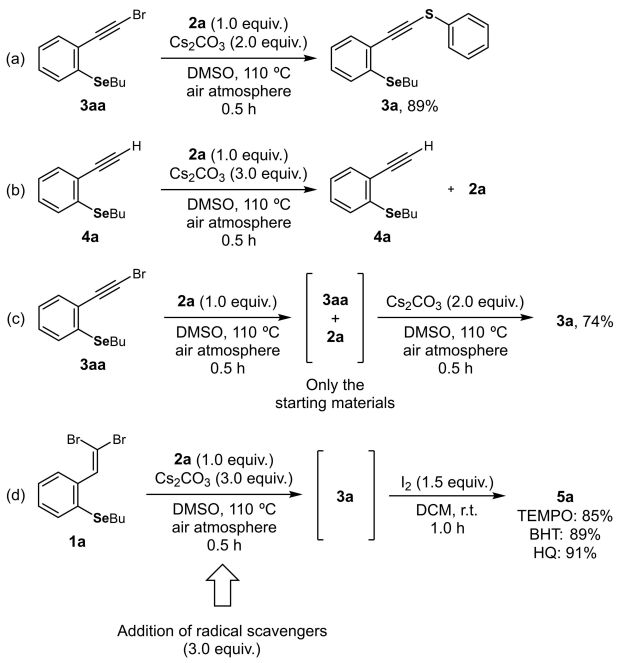
dibromovinyl)-2-organochalcogenylbenzenes (**1a**, **1b** and **1c**) and diphenyl dichalcogenides **2a** and **6a** (Table 4). When these reactions were performed with a higher amount of a stronger electrophile, even the benzo[*b*]furans (**5m**, **8k**) were obtained in moderate yields. The benzo[*b*]thiophenes (**5l**, **8j**) and benzo[*b*] selenophenes (**5k**, **8i**) were also prepared in good yields in up to 2.0 h of reaction at the second step.

In order to clarify the intriguing reaction mechanism of the first step of the one-pot procedure, several experiments were carried out (Scheme 3). Firstly, the reaction between the 1-(2,2-dibromovinyl)-2-butylselanylbenzene (**1a**) and diphenyl disulfide (**2a**) under standard conditions was followed by GC-MS, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy (see figures S1–S4, supporting information). The formation of the respective 1-bromoalkyne **3aa** from a quick base-mediated elimination of **1a** was detected by GC-MS after 0.08 h (5.0 min) of reaction, and trace amounts of the terminal alkyne **4a** were observed after 0.25 h (15 min) of reaction. The formation of **3aa** was also detected by $^{13}C\{^{1}H\}$ NMR spectroscopy after 0.08 h (5.0 min) of reaction, where we observed two characteristic signals at 78.48 ppm and 57.79 ppm, related to both carbons of the triple bond on the 1-bromoalkyne **3aa**. The role of **3aa** as reaction intermediate was supported by an experiment using this compound as starting material with 2.0 equivalents of Cs_2CO_3 (Scheme 3a), which provided 89% isolated yield of **3a**.

On the other hand, when the standard conditions were applied to the terminal alkyne **4a**, only the starting materials were obtained after 0.5 h at 110 °C (Scheme 3b). The role of the base in the following steps was also confirmed by a reaction employing **3aa** and **2a** under the standard conditions of time and temperature, where only the starting materials were detected (Scheme 3c). The intermediate **3a** was obtained in 74% isolated yield only after the addition of 2.0 equivalents of Cs_2CO_3.

Furthermore, the reaction was conducted in the presence of radical scavengers such as TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl), BHT (2,6-di-*tert*-butyl-4-methylphenol) or HQ (hydroquinone) under the standard conditions, and the product **3a** was obtained in 85%, 89% and 91% yields, respectively (Scheme 3d). These data suggests that a radical pathway is not involved in the reaction.

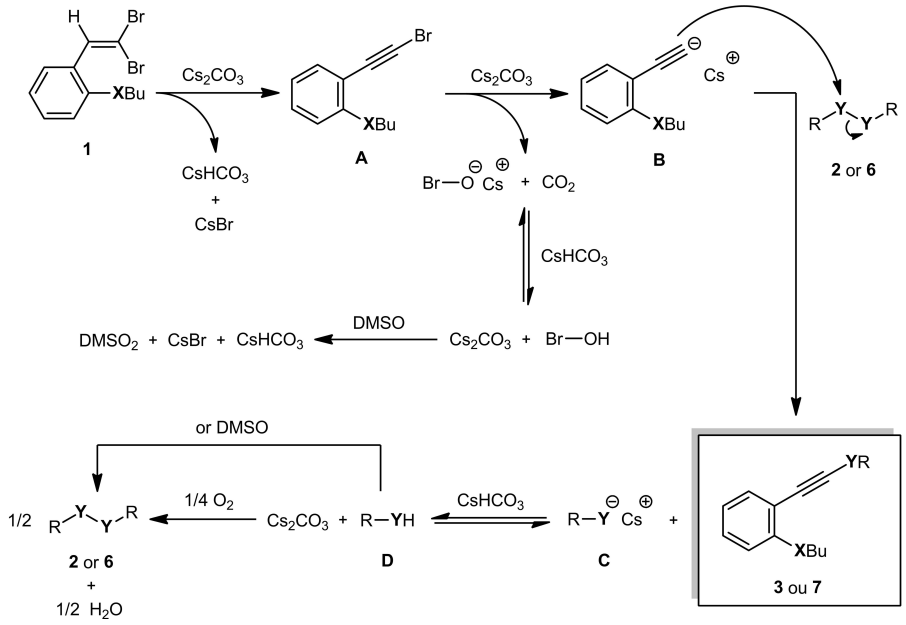
On the basis of our results and the knowledge that 1-bromoalkynes could be a source of acetylide anions in the presence of mild organic or inorganic bases,[22] a plausible mechanism for the first step of this one-pot methodology is proposed in Scheme 4. The reaction initiates through a fast base-promoted elimination of the 1-(2,2-dibromovinyl)-2-organochalcogenylbenzenes (**1**) to generate the respective 1-bromoalkyne (**A**).[23] Subsequently, the umpolung of the key intermediate **A** by Cs_2CO_3 results in the cesium acetylide anion (**B**),[22] which follows a nucleophilic substitution (S_N2) at the X–X bond of the diorganoyl dichalcogenide (**2** or **6**)[24] to produce the expected product (**3** or **7**) and an organochalcogenolate anion (**C**). After this, the diorganoyl dichalcogenide (**2** or **6**) could be regenerated through oxidation of the organochalcogenol (**D**) with O_2,[25] which is in accordance with the air-atmosphere-dependence of this method (Table 1, entry 20). Nevertheless, the oxidation of organochalcogenol (**D**) by DMSO cannot be ruled out.[26] Finally, probably through an acid-base reaction and reduction by DMSO,[27] the cesium hypobromite is quenched in the system.



Scheme 3. Control experiments.

Conclusion

In summary, we have developed a rapid and efficient transition-metal-free method for the synthesis of chalcogenoacetylenes from 1,1-dibromoalkenes. Conceptually, this reaction offers a new approach to trapping diorganoyl dichalcogenides with acetylide anions formed *in situ* from 1,1-dibromoalkenes and mild bases. The conditions of this reaction allowed us to develop a one-pot procedure for the synthesis of 3-halo-2-organochalcogenylbenzo[*b*]chalcogenophenes through an electrophile-promoted nucleophilic cyclization. By using this strategy, we have rapidly achieved the one-pot synthesis of several 2,3-disubstituted benzo[*b*]chalcogenophenes in moderate to excellent yields.



Scheme 4. Proposed reaction steps for the first step of the one-pot methodology.

Experimental Section

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. The reaction solvents DMSO (dimethyl sulfoxide), DMF (*N,N*-dimethylformamide), NMP (*N*-methyl-2-pyrrolidone), DCM (dichloromethane), toluene and ethanol and were dried, purified and degassed by classical methods. Solvents used in liquid-liquid extraction and as eluents for chromatographic purification were distilled before use. The reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F254 aluminum sheets, and the visualization of the spots was by UV light (254 nm) or stained with iodine. Column chromatography was performed on silica gel (230–400 mesh). ^{1}H NMR and ^{13}C NMR were recorded on a 400 MHz Bruker Nuclear Ascend 400 spectrometer and the chemical shifts (δ) reported in parts per million (ppm) relative to TMS as internal standard in spectra made in $CDCl_3$. Coupling constants (*J*) are reported in hertz. Abbreviations to denote the multiplicity of a particular signal on the NMR spectra are described as s (singlet), d (doublet), dt (doublet of triplets), ddd (doublet of doublet of doublets), t (triplet), td (triplet of doublets), q (quartet), quint (quintet), sext (sextet), m (multiplet, complex pattern) and br (broad signal). Melting point (mp) values were measured on a Mettler Toledo MP90 Melting Point System. Low-resolution mass spectra were obtained with a Shimadzu GC-MS-QP2010 Plus mass spectrometer. The single-crystal X-ray diffraction analyses of **5e** (which was obtained by slow evaporation in DMF) were performed at room temperature (rt) on a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector, Mo–Kα radiation (λ = 0.71073 Å) and graphite monochromator. The data were processed using the APEX3 program.[28] The structures were determined by the direct method routines in the SHELXS program[29] and refined by full-matrix least-squares methods, on $F^{2\prime}$s, in SHELXL.[30] The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located in difference maps and were refined isotropically and freely. Scattering factors for neutral atoms were taken from reference.[31] Computer programs used in this analysis have been noted above, and were run through WinGX[32] and figures that refer to the compound **5e** were made using program ORTEP;[32] refinement details can be found in the support information. High resolution mass spectra (HMRS) were recorded in positive ion mode (APCI) using a Bruker micrOTOF-QIII spectrometer.

General procedure for the one-pot synthesis of 3-iodo-2-(organochalcogenyl)benzo[*b*] chalcogenophenes (5a–5i, 8a–8g)

To a Schlenk tube containing the appropriate 1-(2,2-dibromo-vinyl)-2-butylchalcogenylbenzene (**1a–c**) (0.25 mmol, 1.0 equiv.), the dioganyl dichalcogenide (**2a–h**) or (**6a–f**) (0.125 mmol, 1.0 equiv.) was added in dry DMSO (2.0 mL). After this, Cs_2CO_3 (0.244 g, 0.75 mmol, 3.0 equiv.) was added. The reaction system was heated at 110 °C for the reaction time (T1) described on the Tables 2, 3 and 4. After this, the reaction was cooled to room temperature and 1.5 equivalents of I_2 were dissolved in 2 ml of DCM were slowly added (2.0 min). The reaction was stirred at room temperature for the reaction times (T2) described on the Tables 2, 3 and 4. After this, the reaction solution was diluted in water (20 mL) and the excess I_2 was removed by washing the reaction with saturated sodium thiosulfate solution (10 mL). Then, mixture was washed with ethyl acetate (3x 10 mL). The organic phase was dried over magnesium sulfate ($MgSO_4$) and concentrated under reduced pressure. The products were further purified by flash chromatography using hexane as eluent.

3-iodo-2-(phenylsulfanyl)benzo[*b*]benzoselenophene (5a):[17b] Yield: 0,096 g (93%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) = 7.75 (dd, *J* = 8.2 and 1.4 Hz, 1H); 7.62 (dd, *J* = 8.4 and

1.3 Hz, 1H); 7.50–7.48 (m, 2 H); 7,37 (ddd, J=8.2, 7.2 and 1.3 Hz, 1H); 7.34–7.31 (m, 3H); 7,22 (ddd, J=8.4, 7.2 and 1.4 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm)= 143.4, 141.3, 139.8, 134.6, 131.7, 129.4, 128.4, 128.0, 125.7, 125.6, 124.9, 89.2. MS (Rel. Int.) *m/z*: 416 (88.7), 288 (86.1), 208 (100), 77 (22.6).

General procedure for the one-pot synthesis of 3-bromo-2-(organochalcogenyl)benzo[*b*] chalcogenophenes (5 k–5 m, 8 i–8 k)

To a Schlenk tube containing the appropriate 1-(2,2-dibromovinyl)-2-butylchalcogenylbenzene (**1 a–c**) (0.25 mmol, 1.0 equiv.), the dioganyl dichalcogenide (**2 a**) or (**6 a**) (0,125 mmol, 1.0 equiv.) was added in dry DMSO (2.0 mL). After this, Cs_2CO_3 (0.244 g, 0.75 mmol, 3.0 equiv.) was added. The reaction system was heated at 110 °C for the reaction time (T1) described on the Tables 2, 3 and 4. After this, the reaction was cooled to room temperature and 2.5 equivalents of *N*-bromosuccinimide were dissolved in 2 ml of DCM were slowly added (2.0 min). The reaction was stirred at room temperature for the reaction times (T2) described on the Tables 2, 3 and 4. After this, the reaction solution was diluted in water (20 mL) and washed with a saturated sodium thiosulfate solution (10 mL). Then, mixture was washed with ethyl acetate (3x 10 mL). The organic phase was dried over magnesium sulfate ($MgSO_4$) and concentrated under reduced pressure. The products were further purified by flash chromatography using hexane as eluent.

3-bromo-2-(phenylsulfanyl)benzo[*b*]selenophene (5 k):[17b] Yield: 0,072 g (78%); yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm)=7.82 (dd, J=8.1 and 1.0 Hz, 1H); 7.82 (dd, J=8.0 and 1.1 Hz, 1H); 7.54–7.50 (m, 2H); 7.44 (ddd, J=8.1, 7.2 and 1.0 Hz, 1H); 7.39–7.28 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm)=140.3, 140.2, 134.6, 132.0, 131.5, 129.4, 128.4, 125.7, 125.6, 125.5, 125.1, 113.1. MS (Rel. Int.) *m/z*: 367 (78.3), 288 (92.5), 207 (100), 77 (25.8).

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FULL PAPER

One-Pot Synthesis of 3-Halo-2-organochalcogenylbenzo[*b*] chalcogenophenes from 1-(2,2-Dibromovinyl)-2-organochalcogenylbenzenes

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