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Synthesis of 1,3-diarylbenzo[*c*]selenophenes

Arasambattu K. Mohanakrishnan* and P. Amaladass

Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, Tamil Nadu, India

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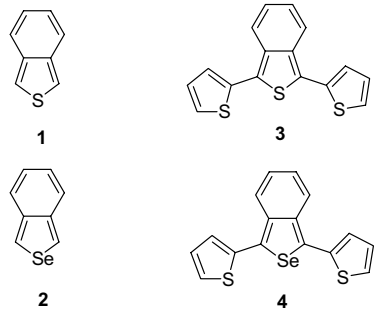
Abstract—For the first time, syntheses of 1,3-diarylbenzo[*c*]selenophenes are reported involving a selenium transfer reaction of keto-alcohol/benzo[*c*]furan using Woollins reagent.

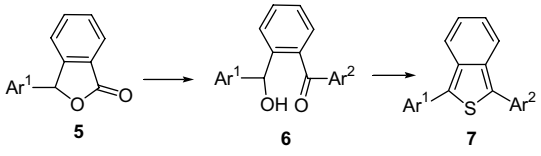
Among the various linear conjugated systems developed, poly(thiophene) derivatives have been paid much attention due to their electronic properties, stability and structural versatility.[1] The synthesis and characterization of benzo[*c*]thiophene **1** analogs are well explored due to the low band gap properties associated with their polymer.[2] In particular, synthetic and electrochemical studies of 1,3-dithienylbenzo[*c*]thiophene **3** (Scheme 1) and its analogs have been well explored.[3] However, the preparation of benzo[*c*]selenophene **2** and its polymers has been explored only to a limited extent. Cava and co-workers reported the synthesis of 1,3-dicyanobenzo[*c*]thiophene and 1,3-dicyanobenzo[*c*]selenophene analogs starting from *o*-xylene dicyanide using $SOCl_2$ and $SeOCl_2$ as sulfur and selenium transfer reagents,[4] respectively. They also reported the synthesis of 1,3-disubstituted benzo[*c*]selenophene analogs,[5] adopting the procedure established for naptho[*c*]thiophenes.[6] Aqad et al. reported the synthesis and electrochemical studies of seleno[3,4-*b*]quinoxalines.[7] The same group also reported[8] the synthesis of methylthio-capped bi-isothianaphthalene and bi-isoselenophene derivatives.

The remarkably low band gap value of poly(benzo[*c*]thiophene) prompted us to explore the synthesis of benzo[*c*]selenophene analogs. Since the synthesis of 1,3-dithienylbenzo[*c*]selenophene **4** (Scheme 1) is yet to be explored, we aimed at the preparation of 1,3-diarylbenzo[*c*]selenophenes which could be reasonably stable. We have recently reported the synthesis of 1,3-diarylbenzo[*c*]thiophenes,[9] including a general procedure from a variety of lactones **5**, which were smoothly converted into the corresponding 1,3-diarylbenzo[*c*]thiophenes **7** via the intermediacy of the keto-alcohol **6** (Scheme 2).



Scheme 1.

A survey of the literature revealed that Woollins reagent $[PhP(Se)(\mu\text{-}Se)]_2$, a selenium analog of well-known sulfur transfer Lawesson reagent, has been used for the preparation of selenoamides.[10] We envisioned that selenium transfer to keto-alcohol **6** followed by cyclization and dehydration similar to diarylbenzo[*c*]thiophene[9] would furnish 1,3-diarylbenzo[*c*]selenophenes. Contrary to the expectation, the reaction of keto alcohol **6a** with 0.25 equiv of Woollins reagent at room temperature



Scheme 2.

Keywords: Benzo[*c*]selenophene; 1,3-Diarylbenzo[*c*]selenophene; Woollins reagent.
* Corresponding author. Tel.: +91 44 24451108; fax: +91 44 22352494; e-mail: mohan_67@hotmail.com

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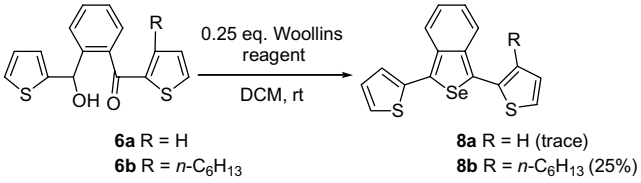


6a R = H
6b R = *n*-C_6H_{13}

8a R = H (trace)
8b R = *n*-C_6H_{13} (25%)

Scheme 3.

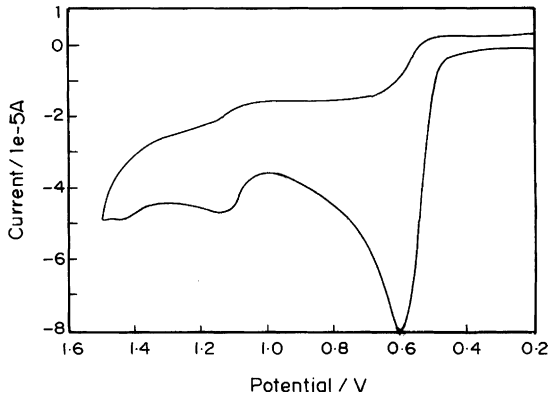
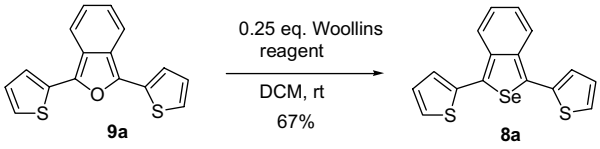


Figure 1. Cyclic-voltammogram of benzo[*c*]selenophene **8a** in acetonitrile solution containing KPF_6 (0.1 M) on a platinum wire electrode (potential relative to Ag/AgCl). Scan rate 100 mV s^{-1}.

for 10 h gave only a trace amount of dithienylbenzo[*c*]selenophene **8a** (M^+ ion at *m*/*z* 345) along with that corresponding to 1,3-dithienylbenzo[*c*]furan (M^+ ion at *m*/*z* 282). However, when ketoalcohol **6b** was interacted with Woollins reagent under identical conditions, 1,3-dithienylbenzo[*c*]selenophene **8b** was formed in 30% yield (Scheme 3). Compound **8b** exhibited satisfactory spectral and analytical data.

Surprisingly, when 1,3-dithienylbenzo[*c*]furan **9**[11] was interacted with Woollins reagent at room temperature in dry DCM for 4 h followed by column chromatographic purification on neutral alumina, benzo[*c*]selenophene **8a** was obtained as an orange solid in 67% yield (Scheme 4).

The synthesis of various 1,3-diarylbenzo[*c*]selenophenes and their yields are summarized in Table 1. The



Scheme 4.

Table 1. Synthesis of benzo[*c*]selenophenes

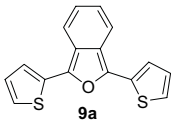
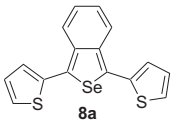
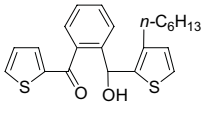
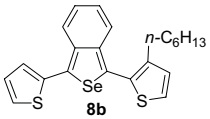
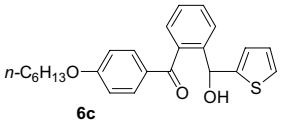
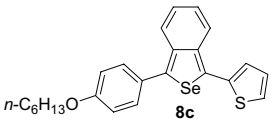
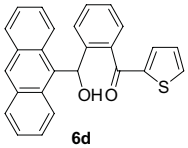
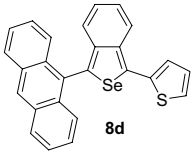
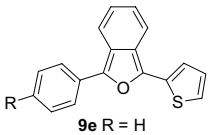
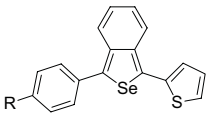
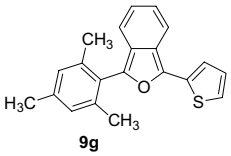
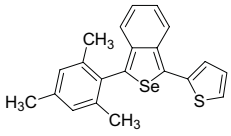
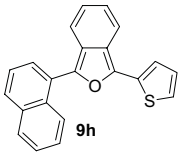
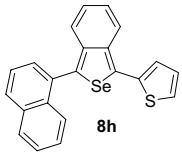
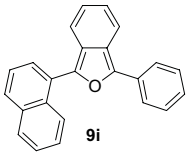
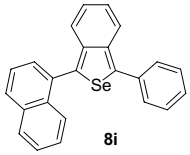
Entry	Keto-alcohol/Benzo[*c*]furan[11]	Products[13]	Yield (%)[a]/mp
1	 **9a**	 **8a**	67 (83 °C)
2	 **6b**	 **8b**	25 (thick liquid)
3	 **6c**	 **8c**	30 (63 °C)
4	 **6d**	 **8d**	20 (162 °C)
5	 **9e** R = H **9f** R = Me	 **8e** R = H **8f** R = Me	62 (thick liquid) 66 (thick liquid)

Table 1 (*continued*)

Entry	Keto-alcohol/Benzo[*c*]furan[11]	Products[13]	Yield (%)[a]/mp
6	 **9g**	 **8g**	60 (thick liquid)
7	 **9h**	 **8h**	58 (92 °C)
8	 **9i**	 **8i**	70 (thick liquid)

[a] Isolated yield after column chromatography.

Table 2. UV spectral data for **8a–i**

Products	**8a**	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**	**8h**	**8i**
λ_{max} (nm) (DCM)	447	422	432	421	427	429	410	418	412

benzo[*c*]selenophenes were obtained in good yields from the respective benzo[*c*]furan, rather than from the keto alcohol. It should be mentioned that 1,3-dithienylbenzo[*c*]furan also underwent the smooth sulfur transfer reaction with Lawesson's reagent to afford the benzo[*c*]thiophene.[3b] All these 1,3-diarylbenzo[*c*]selenophenes are stable and exhibit high fluorescence. The 1,3-diarylbenzo[*c*]selenophenes with at least one free end position could be used for electrophilic substitution, like their benzo[*c*]thiophene analogs.[2e] The UV spectra of benzo[*c*]selenophenes **8a–i** exhibited λ_{max} between 412 and 447 nm and the exact values are given in Table 2. Preliminary cyclic voltammetric analysis of benzo[*c*]selenophene **8a** (Fig. 1) showed an oxidation potential around 0.6 eV.[12]

In summary, for the first time, the synthesis of a range of 1,3-diarylbenzo[*c*]selenophenes has been achieved involving a selenium transfer reaction of a 1,3-diarylbenzo[*c*]furan using Woollins reagent. All these benzo[*c*]selenophene derivatives were well characterized and found to be reasonably stable. Further studies on the electrophilic substitution of benzo[*c*]selenophenes and their electrochemical polymerization are in progress.

Acknowledgements

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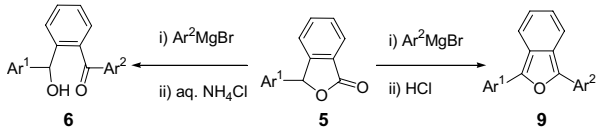
11. The required keto-alcohol **6** and benzo[*c*]furan **9** were prepared from the lactone **5** using the following conditions:



12. The cyclic-voltammogram was carried out under oxygen-free conditions using a solution of benzo[*c*]selenophene **8a** in acetonitrile (10^{-3} M) containing KPF_6 (0.1 M) as supporting electrolyte. The three-component electrode cell consisted of a glassy carbon electrode as a working electrode, saturated Ag/AgCl as reference electrode, and platinum wire as an auxiliary electrode.
13. General procedure for the preparation of benzo[*c*]selenophene from keto-alcohol: The keto-alcohol (1 mmol) and Woollins reagent (0.25 mmol) in dry dichloromethane (20 mL) were stirred for 12 h. After removal of the solvent, the residue was purified by column chromatography (neutral alumina, hexane) to afford the corresponding benzo[*c*]selenophene.

A representative procedure for the preparation of benzo[*c*]selenophenes from benzo[*c*]furans:

Benzofuran **9a** (0.15 g, 0.53 mmol) and Woollins reagent (72 mg, 0.13 mmol) in dry dichloromethane (20 mL) were stirred for 4 h. After removal of the solvent, the residue was purified by column chromatography (neutral alumina, hexane) to afford the benzo[*c*]selenophene **8a** as an orange solid (0.124 g, 67%).

Spectral data of some selected benzo[*c*]selenophenes:

For **8a**: mp 85 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (dd, $J = 3.92$ Hz, $J = 2.92$ Hz, 2H), 7.15 (d, $J = 2.44$ Hz, 2H), 7.40 (d, $J = 3.92$ Hz, 2H), 7.58 (d, $J = 3.44$ Hz, 2H), 7.78 (dd, $J = 3.92$ Hz, $J = 2.92$ Hz, 2H). MS (EI) *m*/*z* (%): 345 (M^+, 13), 253 (44), 208 (31), 127 (26), 84 (100). Anal. Calcd for $C_{16}H_{10}S_2Se$: C, 55.65; H, 2.92; S, 18.57. Found: C, 55.81; H, 3.15; S, 18.81.

For **8b**: (liquid); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.74 (t, $J = 6.8$ Hz, 3H), 1.31–1.60 (m, 8H), 2.53 (t, $J = 7.8$ Hz, 2H), 6.90 (d, $J = 7.8$ Hz, 1H), 6.97 (d, $J = 5.36$ Hz, 1H), 7.05 (dd, $J = 3.6$ Hz, $J = 1.48$ Hz, 1H), 7.22 (dd, $J = 2.44$ Hz, 1.22 Hz, 1H), 7.26–7.30 (m, 4H), 7.76 (d, $J = 8.8$ Hz, 1H). MS (EI) *m*/*z* (%): 430 ($M+1^+$, 100), 360 (10), 277 (24), 215 (25), 85 (14). Anal. Calcd for $C_{22}H_{22}S_2Se$: C, 61.52; H, 5.16; S, 14.93. Found: C, 61.22; H, 5.36; S, 15.22.

For **8c**: mp 63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, $J = 7.1$ Hz, 3H), 1.34–01.38 (m, 2H), 1.45–1.55 (m, 4H), 1.81 (qui, $J = 7.08$ Hz, 2H), 4.01 (t, $J = 6.6$ Hz, 2H), 6.95–7.01 (m, 4H), 7.12 (dd, $J = 3.68$ Hz, $J = 1.44$ Hz, 1H), 7.26 (dd, $J = 2.92$ Hz, $J = 0.98$ Hz, 1H) 7.35 (dd, $J = 4.14$ Hz, $J = 0.98$ Hz, 1H), 7.51 (d, $J = 8.8$ Hz, 2H), 7.59 (d, $J = 9.28$ Hz, 1H), 7.83 (d, $J = 8.8$ Hz, 1H). MS (EI) *m*/*z* (%): 439 (M^+, 54), 356 (43), 215 (77), 111 (53), 57 (100). Anal. Calcd for $C_{24}H_{24}OSSe$: C, 65.59; H, 5.50; S, 7.30. Found: C, 65.81; H, 5.30; S, 7.41.

For **8f**: (liquid); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 6.94–7.00 (m, 3H), 7.02–7.14 (m, 3H), 7.36 (d, $J = 4.88$ Hz, 1H), 7.51 (d, $J = 8.32$ Hz, 2H), 7.63 (d, $J = 8.8$ Hz, 1H), 7.85 (d, $J = 8.8$ Hz, 1H), MS (EI) *m*/*z* (%): 353 (M^+, 5), 251 (72), 145 (13), 129 (100), 105 (52), 57 (63). Anal. Calcd for $C_{19}H_{14}SSe$: C, 64.58; H, 3.99; S, 9.08. Found: C, 64.30; H, 4.19; S, 9.20.

For **8i**: (liquid); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11–7.21 (m, 3H), 7.41–7.58 (m, 2H), 7.61–7.90 (m, 5H), 7.98 (d, $J = 7.36$ Hz, 1H), 8.08 (d, $J = 8.28$ Hz, 2H), 8.17 (d, $J = 7.32$ Hz, 2H), 8.57 (dd, $J = 3.42$ Hz, $J = 2.92$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 119.86, 120.36, 121.52, 123.93, 124.63, 124.69, 125.31, 125.40, 126.13, 126.62, 126.81, 127.33, 128.33, 128.48, 128.95, 129.45, 129.65, 130.96, 131.81, 134.22, 144.41, 144.60. MS (EI) *m*/*z* (%): 383 (M^+, 20), 290 (28), 126 (23), 91 (15), 81 (28). Anal. Calcd for $C_{24}H_{16}Se$: C, 75.20; H, 4.21; Found: C, 74.85; H, 4.35.