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A convenient synthesis of some symmetrical and unsymmetrical diarylmethyl sulfur and selenium compounds: X-ray crystal structure of diphenylmethylseleno-2-propene and bis[*p*-chlorophenyl(phenyl)methyl] diselenide

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Abstract

A number of novel and synthetically important symmetrical and unsymmetrical diarylmethyl sulfur and selenium compounds have been synthesized and characterized with the help of elemental analysis and various spectroscopic techniques. The methodology employs sodium borohydride in ethanol–DMF for E–E bond cleavage (where E = S, Se) at room temperature and gives satisfactory yield of the titled compounds. Molecular structure of bis[*p*-chlorophenyl(phenyl)methyl] diselenide (**3**) and diphenylmethylseleno-2-propene **7** has been established with the help of single crystal X-ray analysis. The compound (**3**) is triclinic and crystallizes into $P\bar{1}$ space group, whereas the compound **7** is monoclinic with $P2_1/C$ space group.

Keywords: Diarylmethyl sulfide/selenide; Hydrazine hydrate; Sodium borohydride; X-ray crystal structure

1. Introduction

Diorganyl selenides are convenient starting materials and excellent synthons in organic synthetic chemistry [1–3]. Among these, the dialkyl selenides are important synthetic targets and valuable precursors for the formation of selenoxides (which undergo thermal or photochemical fragmentation offering routes to many useful and selective functional group transformations). However, despite their potential applications, their wide utilization in diverse areas has largely been restricted due to cumbersome synthetic methodologies, difficulty in purification and unstable nature.

In pursuance of our work on the aliphatic selenium and tellurium compounds, we report herein, a convenient and facile method for the synthesis of some designed bis(diarylmethyl) dichalcogenides and their unsymmetrical monochalcogen derivatives. Some of the properties and decomposition behavior of these compounds have also been discussed.

2. Results and discussion

The synthetic strategy which has been followed to prepare bis(diarylmethyl) disulfides/diselenides, employs hydrazine hydrate as the reducing agent [4]. It is

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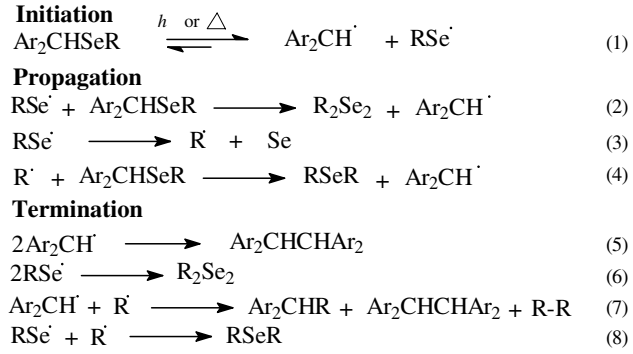
preferred over sodium borohydride because the latter is more expensive and non-selective reagent for the generation of dichalcogenide anions [5]. However, the ditelluride could not be isolated through the same procedure owing to its rapid detelluration, forming largely 1,1,2,2-tetraphenylethane as the coupled product. Attempts to prepare this compound at −30 to −40 °C using sodium metal as a reducing agent in liquid ammonia [6] lead to a transient yellow colored compound which decomposed prior to isolation. The instability of bis(diarylmethyl) ditelluride can be explained on the basis of low bond dissociation energy of a sterically constrained aliphatic C–Te bond.

A scrutiny of the literature shows only one reference, on the synthesis of some unsymmetrical diphenylmethyl selenium compounds, by Kamigata et al. [7]. In this paper the authors have reported the formation of methyl diphenylmethyl selenide (**4**) and benzyl diphenylmethyl selenide (**8**) as side products in the reaction of 1,3-bis(alkylseleno) allenes with diphenyl diazomethane. We have also reported earlier, the synthesis of the corresponding methoxymethyl and ethoxymethyl derivatives [8]. In continuation with the work, we have successfully synthesized a variety of unsymmetrical diarylmethyl selenides and sulfides (**II**) starting from the dichalcogenides (**I**), as shown in the Scheme 1. In this methodology ethanolic sodium borohydride [9] has been used for the reductive cleavage of dichalcogenide bond (E–E) at room temperature. Dimethyl formamide has been employed as a co-solvent in this reaction. Addition of DMF improves the yield by solubilizing the diarylmethyl chalcogenolate anion, which is otherwise known to exist as boron complex possessing diminished nucleophilicity [10].

The various compounds prepared have been characterized through elemental analysis and different spectroscopic techniques viz. NMR (^{1}H, ^{13}C, ^{77}Se, ^{19}F), FT-IR, UV–Vis spectroscopy and mass spectrometry.

It is an interesting observation that most of the *n*-alkyl diphenylmethyl selenides prepared, undergo decomposition over a period of time to form lower symmetrical diselenide of primary alkyl group and 1,1,2,2-tetraphenyl ethane with traces of elemental selenium. Studies

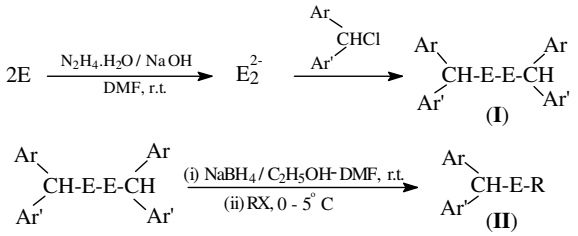


Scheme 2. Proposed mechanism of Ar_2CHSeR decomposition.

conducted by Chu et al. [11,12] on the thermal and photochemical decomposition behavior of dibenzyl diselenide and bis(diphenylmethyl) diselenide reveal a radical mechanism involving C–Se and Se–Se bond scission. A similar analogy can be drawn to comprehend the decomposition behavior of unsymmetrical alkyl diphenylmethyl selenides (Ph_2CHSeR). The primary process is presumed to involve the homolytic cleavage of C–Se bond towards diphenylmethyl carbon (Scheme 2).

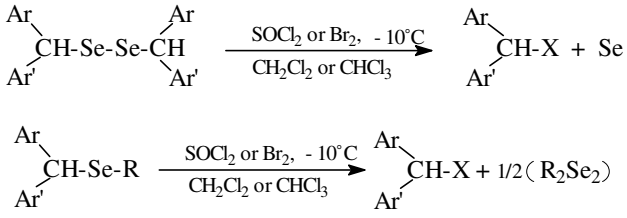
The preferential cleavage of C–Se bond towards diphenylmethyl carbon can be reasonably attributed to the electron delocalization rendered possible by the phenylation of carbon which confers extra stability to the diphenylmethyl radical. The poor stability of C–Se bond may further be discerned from the extensive steric crowding around the selenium atom. On the basis of the products obtained one can say that Eqs. (5) and (6) are major termination pathways.

An attempt to synthesize the bivalent and tetravalent diarylmethyl selenium compounds was not successful through oxidative halogenation of mono- and diselenides. Instead, it resulted in the scission of C–Se bond and diarylmethyl halide was recovered back (Scheme 3). Secondary and tertiary unsymmetrical dialkyl selenides are known to undergo conversion into the corresponding alkyl halides and diselenide of the primary alkyl group [13,14]. We found that the halogenation of



(**I**) E = S, Ar = Ar' = C_6H_5 (**1**); E = Se, Ar = Ar' = C_6H_5 (**2**), Ar = C_6H_5, Ar' = *p*-ClC_6H_4 (**3**); (**II**) E = Se, Ar = Ar' = C_6H_5; R = CH_3 (**4**), C_2H_5 (**5**), n-C_4H_9 (**6**), $CH_2CH{=}CH_2$ (**7**), $CH_2C_6H_5$ (**8**), CH_2CF_3 (**9**), $C_{10}H_7$ (**10**); Ar = C_6H_5, Ar' = p-C_6H_4Cl; R = C_2H_5 (**11**), $CH_2CH{=}CH_2$ (**12**); E = S, Ar = Ar' = C_6H_5; R = C_2H_5 (**13**), $CH_2CH{=}CH_2$ (**14**); X = Br, Cl.

Scheme 1. Reaction scheme for the synthesis of some unsymmetrical diarylmethyl selenides and sulfides.



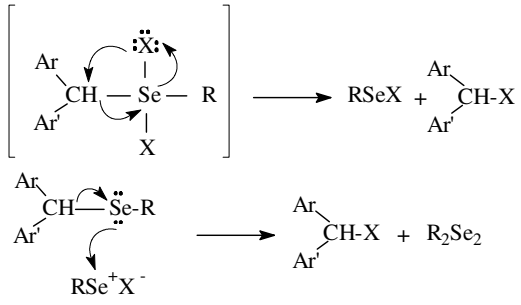
Scheme 3. Halogenation of diphenylmethyl di- and mono-selenides.

n-alkyl diarylmethyl selenides (R = methyl, ethyl, butyl etc.) under similar conditions affords diarylmethyl halides and dialkyl diselenide (R_2Se_2). We assume that the reaction takes place via the formation of electrophilic alkyl selenium species (see Scheme 4).

2.1. Spectroscopic studies

As evident from the NMR data selenium exerts a greater deshielding effect than sulfur, particularly on α-H atoms. The resonance signals of methine protons in all the unsymmetrical diarylmethyl selenides (Ar_2CH-SeR) show a downfield shift of 0.11–0.21 ppm relative to α-H of the corresponding bis(diarylmethyl) diselenide. Nevertheless, the signals appear upfield w.r.t. the methine proton of diarylmethyl chloride (0.7–1.1 ppm). In the ^1H NMR of diphenylmethyl selenides, the absorption signals of aromatic protons display three different sets, two of which are multiplets and the third one, corresponding to the hydrogen at *para* position, appears as a triplet of triplets.

The comparison of spin–spin coupling interactions in allylic derivatives [**7**, **12** and **14**] shows that the magnitude of *trans*-$^3J_{H-H}$ coupling constant of the terminal hydrogen is same in all the three compounds i.e., 16.8 Hz and is much stronger than the *cis*-$^3J_{H-H}$ coupling interaction (which is respectively, 9.6, 10.2 and 9.9 Hz for the compounds **7**, **12** and **14**. The hydrogen *cis* w.r.t vicinal hydrogen experiences greater deshielding than the *trans* hydrogen. In all the cases, the magnitude of coupling constant was found to be consistent with the reported *J* values in allylic systems [15].



Scheme 4. Proposed pathway for the halogenation of unsymmetrical alkyl diphenylmethyl selenides.

The role of a chloro substituent at the *para* positon of the phenyl ring in redistributing the electron density of the ring protons is apparent but not very pronounced. A marginal downfield shift is observed in the *p*-chloro analogues. In case of **9** and **10** the methine carbon is exceptionally deshielded due to the withdrawl of σ-electrons by trifluoromethyl group and naphthyl ring, respectively. ^{13}C NMR spectroscopic results reveal a similar trend, signals corresponding to *ipso*-carbon appear most downfield (139–142 ppm). Other aromatic carbons fall in the region of ca. 126–140 ppm. The chemical shift value of methine carbon is about 51 ppm in case of diselenides and ca. 60 ppm in disulfide. In unsymmetrical monoselenides the absorption occurs in the range of 46–48 ppm. The mass spectrum is rich and complicated due to several isotopes of selenium. For most compounds analyzed the molecular ion peak is either very weak or absent. The fragment corresponding to the mass of diarylmethyl radical is most intense and appears at *m/e* 167 or 202 depending on the aryl substitutents and is assigned the base value. The fragment ions containing selenium show a highly characteristic and definite pattern of signal intensities depending on the natural abundance of various isotopes of selenium.

An evaluation of the ^{77}Se NMR spectra gives a significant insight into the distribution of electron density around selenium metal center. Resonance occurs in the region 259–423 ppm in case of various unsymmetrical diarylmethyl selenides and is sensitive to the variation of substituents on the α-carbon of alkyl group.

2.2. X-ray discussion

To have an understanding of the structural details, single crystal X-ray diffraction of **3** and **7** was carried out. A perspective view and atom numbering scheme of these compounds is given in Fig. 1 and the important bond parameters are listed in Table 1. As observed from the crystallographic data, the geometry of **3** is comparable to **2** given in the literature [16]. The average Se–Se bond distance shows quite normal value. However, the C–Se bond is slightly longer [2.015(4) and 1.995(4) Å] than the expected bond length (1.93–1.97 Å). Unlike few other sterically hindered diselenides [17], the C–Se–Se–C dihedral angle is acute [82.62(18)] and close to the theoretical value [18] of 90° which means that the steric strain is being relieved through bond lengthening rather than widening up of dihedral angle. One common observation in both the crystal structures is that, one of the aryl rings (phenyl or *p*-chlorophenyl) is more closely disposed towards the selenium atom than the other. However, it is evident from the interatomic bond distance comparisons that there are no inter- or intramolecular non-bonded contacts within the crystal lattice. As expected, there is an observed distortion in the

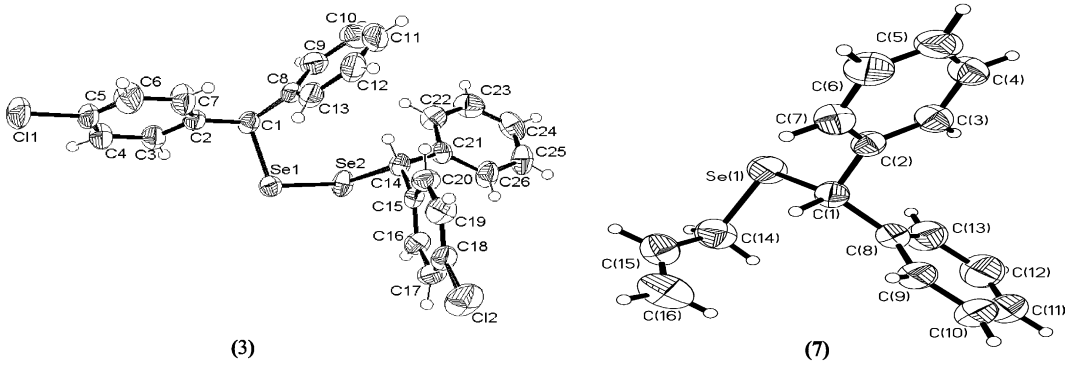


Fig. 1. ORTEP diagram showing the conformation and atom numbering scheme for bis[*p*-chlorophenyl (phenyl)methyl]diselenide (**3**) and diphenylmethylseleno-2-propene (**7**).

Table 1
Selected bond parameters of **3** and **7**

Bond length (Å)		Bond angle (°)		Torsional angle (°)	
Compound (3)					
Se(1)–C(1)	2.015(4)	C(1)–Se(1)–Se(2)	101.31(12)	C(1)–Se(1)–Se(2)–C(14)	82.62(18)
Se(1)–Se(2)	2.3043(7)	C(14)–Se(2)–Se(1)	103.88(11)	Se(2)–Se(1)–C(1)–C(8)	−58.8(3)
Se(2)–C(14)	1.995(4)	C(8)–C(1)–C(2)	117.8(4)	Se(2)–Se(1)–C(1)–C(2)	172.6(2)
Cl(1)–C(5)	1.742(5)	C(8)–C(1)–Se(1)	110.5(3)	Se(1)–Se(2)–C(14)–C(15)	64.5(3)
Compound (7)					
Se(1)–C(1)	1.965(3)	C(1)–Se(1)–C(14)	97.79(13)	C(13)–C(8)–C(1)–C(2)	−89.7
Se(1)–C(14)	1.957(3)	Se (1)–C(1)–C(2)	106.16(17)	C(8)–C(1)–C(2)–C(7)	−137.9
C(1)–C(2)	1.512(4)	Se(1)–C(1)–C(8)	115.6(2)		
C(12)–C(13)	1.397(5)	Se(1)–C(14)–C(15)	110.4(3)		
C(10)–C(11)	1.359(7)	C(14)–C(15)–C(16)	125.9(4)		
C(15)–C(16)	1.293(5)	C(8)–C(1)–C(2)	113.5(2)		

tetrahedral distribution of bond angles around methine carbon in both cases.

In compound **7**, the Se(1)–C(1) and Se(1)–C(14) bond lengths are 1.965(3) and 1.957(3)Å, respectively, which are normal and identified as aliphatic C–Se bonds. The ring [C(8)–C(13)] indicates a small degree of distortion from normal benzene configuration, both in terms of planarity and distribution of bond lengths and bond angles, as evidenced by a slight deviation for C(10)–C(11), C(12)–C(13) bond lengths and C(13)–C(8)–C(9), C(10)–C(9)–C(8) bond angles. Nevertheless, both the rings can be considered to be aromatic and planar within experimental error and this distortion is presumed to arise from different environments around the two rings in the crystal. All other bond parameters show quite normal values.

3. Experimental

All the reactions were carried out under dry and deoxygenated nitrogen atmosphere. Selenium/tellurium were estimated by standard methods [19]. Sodium borohydride (Loba), selenium (Hi-media), elemental sulfur (Aldrich), tellurium (Aldrich) and *p*-chlorophenyl (phenyl)methyl chloride (Aldrich) were newly purchased and stored in a dessicator prior to use. Diphenylmethyl chloride [20] and 1,1′-dinaphthyldiselenide [21] were prepared by literature method. All other chemicals were of analytical grade and used without further purification.

Ethanol was freshly distilled and dehydrated under sodium metal. Other solvents were also purified by standard methods. Melting points were uncorrected. Separation and purification of the compounds was done by column chromatography performed on activated silica gel (230–400) using hexane as eluant.

^{1}H, ^{13}C NMR spectra were recorded in $CDCl_3$ using Me_4Si as an internal standard on JEOL AL 300Mz spectrometer. ^{77}Se and ^{19}F NMR were reported on the same instrument using Me_2Se and $CFCl_3$, respectively, as an external reference. UV–Vis spectral analysis was performed on JASCO V-530 UV–Vis spectrophotometer. Infrared spectra were obtained either between KBr pellets as neat liquids or as compressed KBr discs in case of solid compounds, on a Perkin–Elmer model 1430 spectrophotometer. X-ray diffraction data were collected separately on a Siemens P4 and Nonius MACH3 diffractometer. Elemental analysis was performed on a Perkin–Elmer 2400 CHN analyzer. The mass spectra were obtained on a VG-70S 11-250J mass spectrometer.

3.1. General procedure for the synthesis of bis(diarylmethyl) diselenides/disulfides

To a vigorously stirred mixture of powdered sodium hydroxide (3.0 g, 75 mmol), elemental chalcogen (S = 1.6 g or Se = 4.0 g, 50 mmol) and dimethylformamide (30 ml), 100% hydrazine hydrate was added slowly. After stirring for nearly 6 h at room temperature, a solution of diarylmethyl chloride (100 mmol) dissolved in 15 ml DMF was added dropwise.When the color of solution became light yellow, it was diluted with about 250 ml of distilled water and extracted in dichloromethane (3×50 ml). The organic layer was washed with 6N HCl followed by distilled water and then dried over anhydrous sodium sulfate. The solution was decanted and solvent evaporated to get the crude compound in solid form.The product was purified through recrystallization by dissolving in 5% ethylacetate–hexane.

3.2. General procedure for the synthesis of unsymmetrical diarylmethyl selenides/sulfides

To a 5 mmol solution of bis(diarylmethyl) diselenide/disulfide in 50 ml C_2H_5OH–DMF (3:2) was added 0.456 gm (12 mmol) of $NaBH_4$ in parts with continuous stirring at room temperature. After 3 h of stirring, 10 mmol of the alkylating agent (RX) diluted with equal volume of DMF was added dropwise at 0–5 °C. Reaction was complete within 1–2 h. Extraction is done in dichloromethane after evaporating ethanol under vacuum. The organic layer is washed repeatedly with distilled water (3×40 ml), dried over anhydrous Na_2SO_4. Solvent is evaporated on a rota-evaporator and the product is subjected to purification on a silica column using hexane as the eluant.

3.3. Procedure for the synthesis of **10**

To a vigorously stirred mixture of 1,1′-dinaphthyl diselenide (2.07 g, 5 mmol) and powdered NaOH (1.0 g, 25 mmol) in DMF (30 ml) was added a solution of hydrazine monohydrate (0.3 ml, 6 mmol) in DMF under nitrogen at room temperature. After 2–3 h of stirring, the color of reaction mixture turns pale yellow from orange red. The reaction mixture was then cooled to −10 °C and a solution of diphenylmethyl chloride (1.77 ml, 10 mmol) diluted with equal volume of DMF is added slowly dropwise and stirring continued until the reaction was complete. Extraction was done as in 3.1 and the product was purified on a silica column using hexane as eluant.

3.4. X-ray studies

Diffraction quality single crystals of **3** and **7** were obtained by the slow evaporation of 5% ethylacetate–hexane solution of the compounds. Yellow plate like crystals of **3** were formed in two days. Colorless

Table 2
Crystallographic data and measurements of **3** and **7**

	Compound **3**	Compound **7**
Empirical formula	$C_{26}H_{20}Cl_2Se_2$	$C_{16}H_{16}Se$
Formula Weight (g/mol)	561.24	287.25
Temperature (K)	293(2)	293 (2)
Diffractometer used	Nonius MACH3	Siemens P_4
Radiation used, wavelength (Å)	Mo Kα, 0.70930	Mo Kα, 0.17073
Crystal systems, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/C$
Unit cell dimensions		
a (Å)	9.3750(14)	8.815(1)
b (Å)	9.9780(8)	22.355(1)
c (Å)	12.7900(8)	7.421(1)
α (°)	100.598(6)	90
β (°)	90.188(8)	108.08 (1)
γ (°)	94.062(9)	90
Volume (Å^3)	1172.9(2)	1390.2 (3)
Z, calculated density (Mg/m^3)	2, 1.589	4, 1.372
Absorption coefficient (mm^{-1})	3.391	2.677
F (0 0 0)	556	584
Crystal size	$0.40 \times 0.20 \times 0.15$ mm	$0.22 \times 0.17 \times 0.16$ mm
Index ranges	$0 \leqslant h \leqslant 11, -11 \leqslant k \leqslant 11, 15 \leqslant l \leqslant 15$	$-10 < h < 9, 0 < k < 25, 0 < l < 8$
Reflection collected/unique	3726/3726 [$R_{int} = 0.0000$]	2369/2161 [$R_{int} = 0.0311$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices, [$I > 2\sigma(I)$]	$R_1 = 0.0433$, $\omega R_2 = 0.1055$	$R_1 = 0.0355$, $\omega R_2 = 0.0767$
R indices [all data]	$R_1 = 0.0513$, $\omega R_2 = 0.1147$	$R_1 = 0.0502$, $\omega R_2 = 0.0813$
Largest difference peak and hole (e Å^{-3})	1.227 and −0.924	0.308 and −0.291

cubical crystals of **7** were formed upon cooling saturated solution of this compound. Suitable crystals were chosen from a crop of crystals and mounted on glass fibres and data sets were collected on a Nonius MACH3 diffractometer in case of **3** and Siemens P4 diffractometer in case of **7** for the cell determination and intensity data collection. The diffraction data were collected using monochromatic Mo Kα radiation at 293(2) K. The detail of crystal structure determination and refinement parameters is given in Table 2.

The unit cell parameters were derived and refined by using randomly selected reflections in 2θ range 1.62–24.92 in **3** and 1.82–24.00 in **7**. Crystal structure was solved by direct method (SHELX-97) [22] and refined by full-matrix least-squares method. Anisotropic thermal parameters were employed for non-hydrogen atoms. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

3.4.1. Symmetrical bis(diarylmethyl) dichalcogenides

*3.4.1.1. Bis(diphenylmethyl) disulfide, [$(C_6H_5)_2CHS]_2$ (**1**).* Yield = 77%, colorless crystalline solid, m.p. = 153–154 °C, ^{1}H NMR: δ 7.29 (s, 20H), 4.78 (s, 2H); ^{13}C NMR: δ 140.26, 129.04, 128.52, 127.56, 59.77; IR (KBr, cm^{-1}): 3082.4, 3055.5, 3024.5, 1585.1, 1490.1, 1447.2, 1079.9, 1027.1, 748.1, 719.3, 623.5, 585.9, 525.3; MS-EI, *m/e* (R.I., assignment): 231(0.1, $[Ph_2CHS_2]^+$), 199 (3.7, $[Ph_2CHS]^+$), 167 (100, $[Ph_2CH]^+$), 91 (0.9, $[PhCH_2]^+$); UV–Vis: (C_2H_5OH, λ_{max} nm): 271, 243; (CH_3CN, λ_{max} nm): 397, 310, 272. Anal. Calc. for $C_{26}H_{22}S_2$: C, 78.39; H, 5.52. Found: C, 77.96; H, 5.32%.

*3.4.1.2. Bis(diphenylmethyl) diselenide, [$(C_6H_5)_2CHSe]_2$ (**2**).* Yield = 85%, pale yellow crystalline solid, m.p. = 122–123 °C, ^{1}H NMR: δ 7.22–7.34 (m, 20H), 5.04 (s, 2H); ^{13}C NMR: δ 141.29, 129.20, 128.40 127.23, 51.70; ^{77}Se–NMR: δ 522.2; IR (KBr, cm^{-1}): 3082.6, 3054.9, 3023.7, 1026.3, 999.7, 750.3, 696.7, 613.2, 578.7, 475.0; MS-EI, *m/e* (R.I., assignment): 247 (0.6, $[Ph_2CHSe]^+$), 167 (100, $[Ph_2CH]^+$), 91 (2.8, $[PhCH_2]^+$). Anal. Calc. for $C_{26}H_{22}Se_2$: C, 63.15; H, 4.45. Found: C, 63.02; H, 4.33%.

*3.4.1.3. Bis[p-chlorophenyl(phenyl)methyl] diselenide, [p-$ClC_6H_4(C_6H_5)CHSe]_2$ (**3**).* Yield = 86%, yellow crystalline solid, m.p. = 110–111 °C; ^{1}H NMR: 7.15–7.30 (m, 18H), 4.96 (s, 2H); ^{13}C NMR: δ 140.74, 139.53, 133.39, 130.43, 129.64, 128.72, 128.66, 127.63, 51.08; ^{77}Se–NMR: δ 525.1; IR (KBr, cm^{-1}): 2925.4, 2854.4, 1487.9, 1216.0, 1083.2, 1012.7, 642.6, 598.0, 497.0; MS-EI (*m/e*, R.I., assignment): 282 (0.7, $[C_{13}H_{10}SeCl]^+$), 202 (100, $[C_{13}H_{10}Cl]^+$). Anal. Calc. for $C_{26}H_{20}Se_2Cl_2$: C, 55.41; H, 3.55. Found: C, 54.82; H, 3.24%.

3.4.2. Unsymmetrical alkyl diarylmethyl selenides/alkyldiphenylmethyl sulfides

*3.4.2.1. Methylselenodiphenylmethane, [$Ph_2CHSeCH_3$] (**4**).* Yield = 58%, pale yellow waxy solid, m.p. = 38–45 °C, ^{1}H NMR: δ 7.35–7.38 (m, 4H), 7.21–7.26 (m, 4H), 7.12–7.17 (tt, 2H), 5.25 (s, 1H), 1.79 (s, 3H); ^{13}C NMR: δ 141.55, 128.82, 128.52, 126.99, 48.81, 6.22; ^{77}Se–NMR: δ 259.5; IR (KBr, cm^{-1}): 3026.0, 3001.5, 2923.7, 1375.3, 1448.7, 580.4, 624.0; MS-EI (*m/e*, R.I., assignment): 262 (0.2, $[M]^+$), 247 (0.6, $[Ph_2CHSe]^+$), 167 (100, $[Ph_2CH]^+$). Anal. Calc. for $C_{14}H_{14}Se$: C, 78.39; H, 5.52. Found: C, 77.96; H, 5.32%.

*3.4.2.2. Ethylselenodiphenylmethane, [$Ph_2CHSeCH_2CH_3$] (**5**).* Yield = 65%, yellow oil, ^{1}H NMR: δ 7.26–7.30 (m, 4H), 7.11–7.16 (m, 4H), 7.00–7.06 (tt, 2H), 5.26 (s, 1H), 2.20–2.31 (q, 2H, 7.5 Hz), 1.19–1.25 (t, 3H, 7.5 Hz); ^{13}C NMR: δ 141.79, 128.84, 128.46, 126.90, 47.30, 19.20, 15.36; ^{77}Se–NMR: δ 376.7; IR (KBr, cm^{-1}): 3083.3, 3059.9, 3024.9, 2956.3, 2922.7, 2865.6, 1598.8, 1582.4, 1493.2, 1448.0, 964.9, 623.8, 581.0. Anal. Calc. for $C_{15}H_{16}Se$: C, 65.21; H, 5.79. Found: C, 65.45; H, 5.38%.

*3.4.2.3. n-Butylselenodiphenylmethane, [$Ph_2CHSeC_4H_9$] (**6**).* Yield = 65%, yellow oil, ^{1}H NMR: δ 7.25–7.29 (m, 4H), 7.08–7.14 (m, 4H), 6.97–7.03 (tt, 2H), 5.22 (s, 1H), 2.20–2.25 (t, 2H, 7.5 Hz), 1.38–1.48 (m, 2H), 1.13–1.26 (m, 2H), 0.69–0.74 (t, 3H, 7.2 Hz); ^{13}C NMR: δ 141.87, 128.83, 128.44, 126.88, 47.55, 32.13, 25.15, 23.15, 13.82; ^{77}Se–NMR: δ 344.5; IR (KBr, cm^{-1}): 3025.1, 3001.3, 2956.5, 2925.9, 2870.4, 1493.5, 1378.0, 1448.3, 623.5, 580.3. Anal. Calc. for $C_{17}H_{20}Se$: C, 67.10; H, 6.57. Found: C, 66.84; H, 6.12%.

*3.4.2.4. Allylselenodiphenylmethane, [$Ph_2CHSeCH_2CH{=}CH_2$] (**7**).* Yield = 70%, colorless crystalline solid, m.p. = 46–47 °C; ^{1}H NMR: 7.40–7.43 (m, 4H), 7.21–7.26 (m, 4H), 7.11–7.17 (tt, 2H), 5.78–5.92 (m, 1H), 5.32 (s, 1H), 4.91–4.94 (d, 1H, 9.6 Hz), 4.68–4.75 (dd, 1H, 16.8 Hz, 2.4 Hz), 2.86–2.89 (d, 2H, 7.5 Hz); ^{13}C NMR: δ 141.21, 134.65, 128.84, 128.29, 126.73, 116.17, 47.18, 27.97; ^{77}Se–NMR: δ 366.6; IR (KBr, cm^{-1}): 3062.4, 3026.7, 2924.5, 2853.6, 1493.5, 1427.5, 1628.0, 624.4, 580.0; MS-EI, *m/e* (R.I., assignment): 288(0.1, $[M]^+$), 247 (0.6, $[Ph_2CHSe]^+$), 207 (0.6, $[M-Se]^+$), 167 (100, $[Ph_2CH]^+$). Anal. Calc. for $C_{16}H_{16}Se$: C, 66.66; H, 5.55. Found: C, 67.31; H, 5.62%.

*3.4.2.5. Benzylselenodiphenylmethane, [$Ph_2CHSeCH_2Ph$] (**8**).* Yield = 75%, colorless crystalline solid, m.p. = 51–52 °C; ^{1}H NMR: 7.31–7.34 (d, 4H), 7.04–7.29 (m, 11H), 5.15 (s, 1H), 3.47 (s, 2H); ^{13}C NMR: δ 141.34, 138.99, 129.12, 129.07, 128.54, 128.37, 127.01, 126.70, 47.96, 29.56; ^{77}Se–NMR: δ 422.5; IR (KBr, cm^{-1}): 3027.9, 2926.4, 2854.2, 1419.8, 1451.0, 626.1,

580.2. Anal. Calc. for $C_{19}H_{18}Se$: C, 71.00; H, 5.32. Found: C, 71.86; H, 5.22%.

*3.4.2.6. 2,2,2-Trifluoroethylselenodiphenylmethane, [$Ph_2CHSeCH_2CF_3$] (**9**).* Yield = 70%, golden yellow oil, ^{1}H NMR: δ 7.42–7.45 (m, 4H), 7.26–7.31 (m, 4H), 7.18–7.23 (tt, 2H), 5.62 (s, 1H), 2.71–2.82 (q, 2H, 10.6 Hz); ^{13}C NMR: δ 139.82, 128.74, 128.72, 127.57, 126.4 (q, −279.3 Hz; δ 120.9, 124.6, 128.2, 131.8), 48.59, 25.6 (q, 32.9 Hz; δ 24.9, 25.4, 25.8, 26.2);^{77}Se–NMR: 313.3; FT-IR (KBr, cm^{-1}): 3062.8, 3028.7, 2925.1, 2854.2, 1749.0, 1599.6, 1494.3, 1450.0, 1290.4, 1259.5, 1031.6, 631.4, 581.4, 518.1; ^{19}F NMR: δ − 63.83 (triplet, 7.63 Hz). Anal. Calc. for $C_{13}H_{13}SeF_3$: C, 50.98; H, 4.24. Found: C, 49.86; H, 4.00%.

*3.4.2.7. 1-Naphthylselenodiphenylmethane, [$Ph_2CHSeC_{10}H_7$] (**10**).* Yield = 70%, pale yellow crystalline solid, m.p. = 70–71 °C, ^{1}H NMR: δ 8.39–8.41 (d, 1H, 8.4 Hz), 7.72– 7.75 (d, 1H, 8.1 Hz), 7.66–7.69 (d, 1H, 8.4 Hz), 7.39–7.50 (m, 3H), 7.23–7.29 (m, 4H), 7.08–7.20 (m, 7H), 5.54 (s, 1H); ^{13}C NMR: δ 141.52, 134.91, 134.60, 134.04, 129.00, 128.85, 128.65, 128.40, 128.24, 128.11, 127.03, 126.68, 126.06, 125.64, 52.69; UV–Vis (C_2H_5OH, λ_{max}): 287, 319, 327 nm; (CH_3CN, λ_{max}): 327 nm; ^{77}Se–NMR: δ 407.2; FT-IR (KBr, cm^{-1}): 3029.1, 3058.4, 2924.5, 2853.9, 1654.3, 1599.6, 1494.1, 1449.3, 1031.3, 962.1, 616.4, 581.1. Anal. Calc. for $C_{21}H_{18}Se$: C, 72.00; H, 5.14. Found: C, 71.86; H, 4.98%.

*3.4.2.8. Ethylseleno(p-chlorophenyl)phenylmethane, [(p-ClC_6H_4)$C_6H_5CHSeCH_2CH_3$] (**11**).* Yield = 60%, yellow oil, ^{1}H NMR: δ 7.21–7.27 (m, 4H), 7.05–7.17 (m, 5H), 5.22 (s, 1H), 2.22–2.29 (q, 2H, 7.5 Hz), 1.18–1.23 (t, 3H, 7.5 Hz); ^{13}C NMR: δ 141.12, 140.25, 132.68, 129.94, 128.59, 128.54, 128.47, 127.02, 46.33, 19.22, 15.18; FT-IR (KBr, cm^{-1}): 3061.2, 3024.5, 2895.3, 1577.0, 1468.4, 1413.6, 602.7, 512. Anal. Calc. for $C_{15}H_{15}SeCl$: C, 57.97; H, 3.86. Found: C, 57.24; H, 3.23%.

*3.4.2.9. Allylseleno(p-chlorophenyl)phenylmethane, [(p-ClC_6H_4)$C_6H_5CHSeCH_2CH{=}CH_2$] (**12**).* Yield = 68%, white crystalline solid, m.p. = 41–42 °C; ^{1}H NMR: δ 7.28–7.38 (m, 4H), 7.18–7.25 (m, 4H), 7.11–7.16 (m, 1H), 5.75–5.90 (m, 1H), 5.21 (s, 1H), 4.91–4.95 (d, 1H, 10.2 Hz), 4.75–4.80 (d, 1H, 16.8 Hz), 2.93–2.95 (d, 2H, 7.5 Hz); ^{13}C NMR: δ 140.81, 139.96, 134.57, 132.72, 130.24, 128.87, 128.66, 128.61, 127.18, 116.56, 46.43, 28.28; FT-IR (KBr, cm^{-1}): 3084.4, 2924.5, 1632.7, 1597.6, 1488.8, 1451.2, 1428.0, 1014.9, 988.4, 756.2, 719.1, 601.3, 505.3; ^{77}Se–NMR: δ 368.2. Anal. Calc. for $C_{16}H_{15}SeCl$: C, 59.53; H, 4.65. Found: C, 58.76; H, 4.38%.

*3.4.2.10. Ethylthiodiphenylmethane, [$Ph_2CHSCH_2CH_3$] (**13**).* Yield = 65%, colorless oil, ^{1}H NMR: δ 7.25–7.29 (m, 4H), 7.12–7.19 (m, 4H), 7.03–7.08 (tt, 2H), 5.01 (s, 1H), 2.22–2.24 (q, 2H, 7.5 Hz), 1.07–1.12 (t, 3H, 7.5 Hz); ^{13}C NMR: δ 141.58, 128.453, 127.051, 53.96, 26.17, 14.33; FT-IR (KBr, cm^{-1}): 3060.6, 3026.0, 2965.9, 2870.3, 1599.7, 1493.7, 1449.1, 1030.3, 1002.3, 749.1, 700.9, 628.8, 585.9, 506.6. Anal. Calc. for $C_{15}H_{16}S$: C, 78.94; H, 7.01. Found: C, 78.26; H, 6.98%.

*3.4.2.11. Allylthiodiphenylmethane, [$Ph_2CHSCH_2CH{=}CH_2$] (**14**).* Yield = 80%, colorless crystalline solid, m.p. = 44–45 °C; ^{1}H NMR: 7.27–7.29 (m, 4H), 7.15–7.20 (m, 4H), 7.06–7.11 (tt, 2H), 5.65–5.75 (m, 1H), 4.98–5.01 (d, 2H, 9.9 Hz), 4.97 (s, 1H), 4.84–4.90 (dd, 1H, 16.8 Hz, 1.8 Hz), 2.87–2.89 (d, 2H, 6.9 Hz); ^{13}C NMR: δ 141.28, 134.25, 128.74, 128.55, 127.16, 117.29, 52.85, 35.14; FT-IR (KBr, cm^{-1}): 3084.9, 3064.1, 3028.2, 2916.9, 1635.7, 1599.8, 1494.7, 1450.1, 1031.1, 990.2, 630.4, 585.5, 504.8. Anal. Calc. for $C_{16}H_{16}S$: C, 80.00; H, 6.66. Found: C, 79.96; H, 6.34%.

4. Supplementary material

Crystallographic information (excluding structure factors) have been deposited in the CIF (Crystallographic Information File) format with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 234297 and 190931 for the compounds (**3**) and (**7**), respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB21E2, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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