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An indium–TMSCl promoted reaction of diphenyl diselenide and diorganyl disulfides with aldehydes: novel routes to selenoacetals, thioacetals and alkyl phenyl selenides

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ABSTRACT

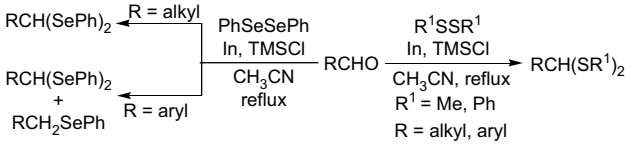
The reactions of diphenyl diselenide and dialkyl disulfides with aldehydes in the presence of In–TMSCl have been investigated. Aliphatic aldehydes provide the corresponding selenoacetals and aromatic aldehydes lead predominantly to benzyl phenyl selenides on reaction with diphenyl diselenide. However, the reaction of dimethyl disulfide and diphenyl disulfide with both aromatic and aliphatic aldehydes produce dithioacetals. This provides a novel route to the synthesis of selenoacetals, thioacetals and selenides from aldehydes.

1. Introduction

Indium metal and its derivatives have been found to have great potential for organic transformations and have generated new interesting chemistry.[1] As a part of our continued activities to develop novel synthetic procedures using indium and indium derivatives,[1e,2] recently we have communicated an interesting reaction of diphenyl diselenide with aldehydes promoted by In–TMSCl.[2r] Aliphatic aldehydes provided the corresponding selenoacetals, whereas aromatic aldehydes produced predominantly benzyl phenyl selenides under the same reaction conditions. This prompted us to investigate the scope of this reaction in more detail and we considered to study the reaction of dialkyl disulfides and aldehydes in the presence of In–TMSCl. In contrast to the results with diphenyl diselenide we observed uniform formation of dithioacetals from both aliphatic and aromatic aldehydes using dimethyl disulfide and diphenyl disulfide. We report here the detail of our earlier communication[2r] with inclusion of a few more aldehydes and the recent results of reaction with disulfides (Scheme 1).

2. Results and discussion

The experimental procedure is very simple. A mixture of diphenyl diselenide/dialkyl disulfide, an aldehyde and trimethylsilyl chloride in acetonitrile was heated under reflux in the presence of indium metal for a period of time (Tables 1 and 2). Standard work-up and extraction with ether provided the product. A wide range of structurally diverse aliphatic and aromatic aldehydes underwent reactions with diphenyl diselenide by this procedure to produce the corresponding products. The results are summarized in Table 1. All the aliphatic aldehydes produced the corresponding selenoacetals (entries 1–7, Table 1) whereas the aromatic aldehydes furnished exclusively (entries 8–15, Table 1) or predominantly (entries 16–18, Table 1) the corresponding benzyl phenyl selenides. In sharp contrast, 4-fluorobenzaldehyde produced more selenoacetal than selenide (entry 19, Table 1). Although, in general halo-substituted benzaldehydes led to mixtures



Scheme 1. Reaction of aldehydes with diselenides/disulphides in presence of In–TMSCl.

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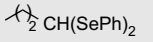
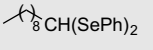
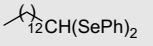
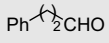
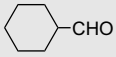
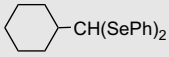
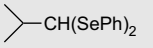
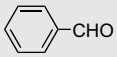
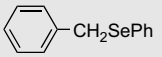
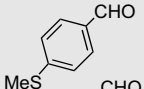
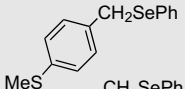
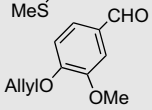
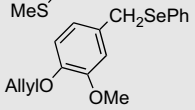
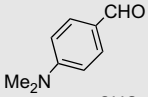
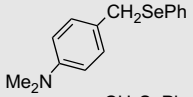
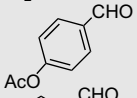
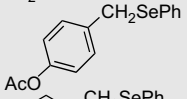
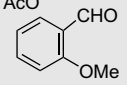
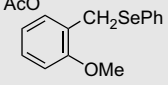
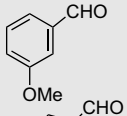
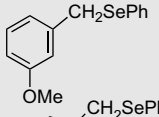
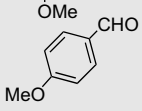
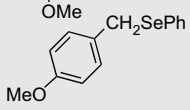
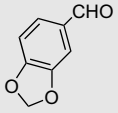
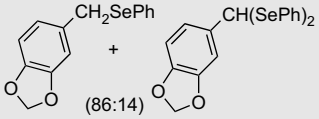
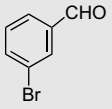
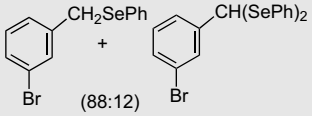
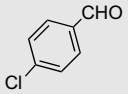
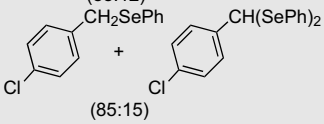
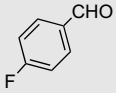
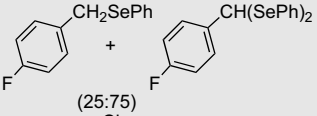
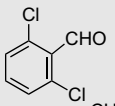
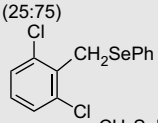
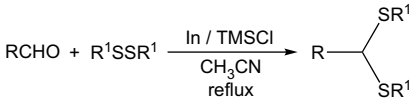
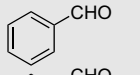
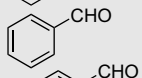
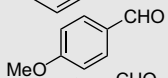
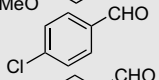
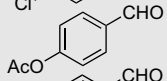
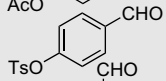
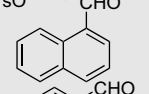
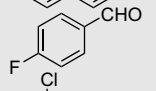
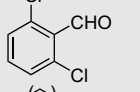
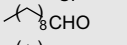
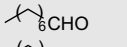
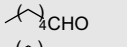
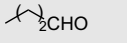
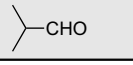
Table 1
Indium–TMSCl promoted reaction of aldehydes with diphenyl diselenide

Entry	Aldehyde	Time (h)	Product	Yield[a] (%)	Ref.
1		2.0		70	
2		2.5		78	
3		2.5		72	
4		2.5		76	
5		4.5		75	
6		2.0		71	
7		2.0		80	
8		7.0		75	2j
9		5.5		76	
10		3.5		72	
11		2.5		65	
12		2.5		75	
13		3.0		73	
14		3.5		72	
15		3.5		74	
16		4.0	 (86:14)	80	2j
17		7.0	 (88:12)	70	
18		6.5	 (85:15)	75	2j
19		6.0	 (25:75)	65	
20		6.0		63	14
21		5.5		72	

[a] Yields refer to those of pure and isolated products characterized by IR, ^{1}H and ^{13}C NMR spectroscopic data.

Table 2
Indium–TMSCl promoted protection of aldehydes as dithioacetals

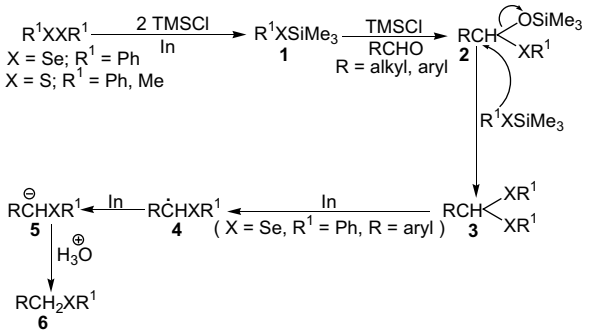


Entry	Aldehyde	Disulfide	Time (h)	Yield[a] (%)	Ref.
1		MeSSMe	2	76	15
2		PhSSPh	3	70	16
3		MeSSMe	2	73	15
4		MeSSMe	2	72	15
5		MeSSMe	1.5	67	
6		MeSSMe	2	68	
7		MeSSMe	2.5	65	17
8		MeSSMe	3	78	
9		MeSSMe	4	73	
10		MeSSMe	2	70	18
11		PhSSPh	3	69	19
12		PhSSPh	2	72	20
13		PhSSPh	2	75	21
14		PhSSPh	2	73	19

[a] The yields refer to those of pure isolated products characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopic data.

of selenoacetals and selenides, 2,6-dichlorobenzaldehyde provided the corresponding selenide as the only isolable product (entry 20, Table 1), probably due to steric inhibition by two adjacent Cl groups. It was found that an isolated pure selenoacetal of 3-bromobenzaldehyde was converted to the corresponding selenide under the same reaction conditions after 6 h. Thus, in the reactions of aromatic aldehydes where a mixture of benzyl phenyl selenides and selenoacetals was produced, the proportion of selenides was increased at the cost of selenoacetals after longer periods although 100% conversion was not achieved. When the reactions of aliphatic aldehydes were allowed to proceed for longer periods, no alkyl selenides were obtained. Thus, it is likely that the reactions of aliphatic aldehydes stopped at the selenoacetal stage whereas reactions of aromatic aldehydes proceeded further to produce selenides. Based on these observations we propose a mechanism as outlined in Scheme 2.

Several aromatic and aliphatic aldehydes underwent reactions with dialkyl and diaryl disulfide by this procedure to provide the corresponding dithioacetals. The results are summarized in Table 2. The reaction was uniform with aromatic as well aliphatic aldehydes. Several functionalities present in the aromatic ring such as OMe, OTs, OAc, Cl, F are compatible with the reaction conditions. The nature of substitution at the aromatic ring did not make much difference in reactivity and yields. Dimethyl disulfide reacted with several aromatic and aliphatic aldehydes (entries 1, 3–10, Table 2)



Scheme 2. Probable mechanism.

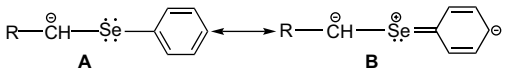
producing the corresponding dimethylthioacetals, which are difficult to achieve using gaseous methanethiol by conventional procedures.

In general, the reactions were clean and reasonably fast. The products were obtained in high purities. Although a few aromatic aldehydes (entries 16–19, Table 1) led to mixtures of selenides and selenoacetals these could be separated by careful column chromatography. All the compounds were characterized by their spectroscopic data. The reaction did not proceed at all either in absence of TMSCl or indium metal. The combination of In and TMSCl is thus essential for this reaction. The replacement of TMSCl by $BF_3\cdot Et_2O$ also did not produce any result. Acetonitrile was found to provide the best results in terms of yields and reaction time compared to other solvents like THF and dioxane.

It is suggested that indium cleaves the diselenide/disulfide bond to form a transient indium–selenoate/thiolate complex, which on reaction with TMSCl produces alkylseleno/thiotrimethylsilane **1** (R^1XSiMe_3),[3] which then interacts with the aldehyde to give the intermediate **2**, ultimately leading to diseleno/thioacetal **3**, as outlined in Scheme 2. The formation of R^1XSiMe_3 was indicated by the presence of the corresponding molecular ion peak (183.0368 for M+H) in HRMS of a sample from the reaction mixture of PhSSPh and In–TMSCl in dry CH_3CN. Possibly, TMSCl acts as Lewis acid during the formation of the intermediate **2** activating aldehydes towards nucleophilic attack by R^1XSiMe_3. As indium metal is well known one-electron reducing agent it is more likely that selenoacetal **3** undergoes homolytic cleavage followed by anion formation to lead to selenides **6** in reactions of aromatic aldehydes. The intermediacy of a free radical species gains support when we found that a radical quencher considerably affects the course of the reaction of aromatic aldehydes. Thus, when the reaction of 2-methoxybenzaldehyde (entry 13, Table 1) was carried out in presence of a quencher, 4-hydroxy TEMPO under reflux for 5 h, the formation of the corresponding selenide was considerably diminished; a 1:1 mixture of selenoacetal and selenide being obtained whereas in the normal reaction the selenide was obtained as the only isolable product after 3 h. In contrast, the quencher had no effect on the conversion of an aliphatic aldehyde (decanal, entry 3, Table 1) to the selenoacetal.

In diphenyl diselenide reactions (X=Se, Scheme 2) the stability of the benzylic radical **4** determines the further progress of the reaction. Thus, the reaction of aromatic aldehydes (R=Ph) in general ended in the formation of selenides. The aliphatic aldehydes being unable to provide this stability stopped at the selenoacetal stage. In reactions with dialkyl disulfides (X=S, Scheme 2) the homolytic cleavage of **3** is not as facile as in selenide reactions, probably because of the higher polarity of C–S bond compared to C–Se bond[4] and the lower stability of the thio-carbanion **5** (X=S) compared to seleno-carbanion. The seleno-carbanion also acquires more stability having appreciable contribution from the resonance structures **A** and **B**.[4] On the other hand, sulfur being considerably

more electronegative this type of resonance stabilization is unlikely. Thus, reaction of dialkyl disulfides did not go further and ended with the formation of thioacetal.



Selenoacetals are versatile intermediates in organic synthesis and have played a crucial role in the development of organoselenium chemistry.[5] They are stable in basic and mildly acidic conditions, inert to Grignard reagents and thus have similar properties to their oxygen and sulfur analogues. They can also be useful for carbonyl protection.[5] Usually, selenoacetals are prepared from the corresponding carbonyl compounds by reaction with selenols or [$B(SeMe)_3$] under the catalysis of protic or Lewis acids.[6] Alternatively, they can be prepared by exchange reactions between *O*-acetals and tris(phenylseleno)borane.[7] However, all these reagents—selenols and tris(alkylseleno)borane—are usually prepared from dialkyl diselenides.[6] Thus, the present procedure involving diphenyl diselenide would be more convenient and practical.

Organic selenides are of considerable interest in academia as well as in industry because of their wide involvement in organic synthesis[8a] and their biological actitivies.[8b] Although a number of procedures for the synthesis of dialkyl/alkyl aryl selenides have been reported[9] most of them use alkyl halides as starting materials. To the best of our knowledge no method is available starting from aldehydes. Thus the present protocol (Scheme 1) provides new routes for the synthesis of selenoacetals and benzyl phenyl selenides.

Among various carbonyl protecting groups dithioacetals are preferred because of their inherent stability under both acidic and basic conditions.[10] In addition, dithioacetals are also used as precursors for acyl anions and as intermediates in the conversion of a carbonyl group into a hydrocarbon derivative.[11] A number of procedures using thiols and a variety of protic and Lewis acids, metal salts as catalysts have been developed for thioacetalization of carbonyl compounds. The catalysts employed are perchloric acid supported on silica,[12a] Amberlyst-15,[12b] $RuCl_3$,[12c] *p*-TsOH on silica gel,[12d] $Pr(OTf)_3$,[12e] $Sc(OTf)_3$,[12f] $MoO_2(acac)_2$,[12g] $NiCl_2$,[12h] NBS,[12i] $InCl_3$,[12j] tungstophosphoric acid,[12k] $InBr_3$,[12l] LiOTf,[12m] tetrabutylammonium bromide,[12n] among others. Many of these procedures were associated with drawbacks such as low yields and long reaction time. Moreover, a couple of practical disadvantages regarding handling of thiols are their inherent foul odour and gaseous state for methanethiol. Thus, thiol-free alternative methods using stable (solid/liquid) dialkyl disulfides having relatively less odour are appreciated and procedures using dialkyl disulfide and tributylphosphine,[13a] methylthiotrimethylsilane[3] have been introduced. However, use of tributylphosphine entails a waste of tributylphosphine oxide and purification of products from tributylphosphine oxide is also very tedious. The other reagent, methylthiotrimethylsilane is very expensive. On the other hand, this is highly moisture sensitive and very difficult to prepare.[3] Thus, our procedure of thioacetal formation from aldehydes using dialkyl disulfide provides a better alternative.

3. Conclusion

In conclusion, the present procedure using the In–TMSCl provides a new route for the synthesis of selenoacetals, thioacetals and benzyl phenyl selenides from aldehydes. The significant features of this procedure are (a) simple one-pot operation, (b) use of stable and readily available diselenide and disulfides as reagents, (c) reasonably fast reaction and (d) good isolated yields of products. Most significantly, these procedures present a novel protocol for access to benzyl phenyl selenides from aromatic aldehydes and an alternative thiol-free process for dithioacetalization of aldehydes providing a practical alternative to the preparation of dimethylthioacetal, difficult to achieve by conventional methods using methanethiol. Moreover, it demonstrates further potential of In–TMSCl reagent for organic transformations.

4. Experimental

4.1. General

Indium metal (SRL, India), cut into small pieces was used for all reactions. Trimethylchlorosilane was freshly distilled before use. IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 300 and 75 MHz, respectively. Elemental analysis was done using a Perkin–Elmer autoanalyzer at IACS.

4.1.1. General experimental procedure for the synthesis of selenoacetals and aryl phenyl selenides. Representative procedure for 1,1-diphenylselenooctane (entry 2, Table 1)

To a stirred solution of diphenyl diselenide (1 mmol, 312 mg) and trimethylsilyl chloride (2 mmol, 218 mg) in dry acetonitrile (3 mL) was added octanal (1 mmol, 128 mg) and the mixture was stirred for 2 min at room temperature. The reaction mixture was then heated under reflux with indium metal (1 mmol, 115 mg, cut into small pieces) for 2.5 h (TLC). After completion of the reaction acetonitrile was evaporated off in vacuo and the residue was extracted with ether (10×3 mL). The combined ether extract was then washed with brine, dried (Na_2SO_4) and evaporated to leave the crude product, which was purified by column chromatography over silica gel (hexane–ether 98:2) to furnish the pure 1,1-diphenylselenooctane as a yellow liquid (331 mg, 78%). IR (neat): 1436, 1475, 1578 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ: 0.78 (t, J=6.6 Hz, 3H), 1.13–1.18 (m, 7H), 1.46–1.49 (m, 3H), 1.80–1.89 (m, 2H), 4.40 (t, J=6.5 Hz, 1H), 7.16–7.22 (m, 6H), 7.48–7.51 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ: 13.9, 22.5, 28.2, 28.7, 28.9, 31.6, 36.9, 44.0, 127.8 (2C), 128.9 (4C), 130.3 (2C), 134.5 (4C). Anal. Calcd for $C_{20}H_{26}Se_2$: C, 56.61; H, 6.18. Found: C, 56.37; H, 6.03.

This procedure was followed for all the aldehydes listed in Table 1. As mentioned earlier aliphatic aldehydes produced the corresponding selenoacetals (entries 1–7, Table 1) and aromatic aldehydes provided benzyl phenyl selenides (entries 8–15, 20, 21, Table 1) or mixtures of benzyl phenyl selenides and selenoacetals (entries 16–19, Table 1). The known compounds (entries 8, 16, 18, 20, Table 1) were identified by comparison of their spectral data with those reported (Table 1), and the new compounds (entries 1–7, 9–15, 17, 19, 21, Table 1) were properly characterized by their IR, ^1H NMR and ^{13}C NMR spectroscopic data and elemental analysis. The data for these compounds are presented below.

4.1.2. 1,1-Diphenylseleno butane (entry 1, Table 1)

A yellow liquid; IR (neat): 1437, 1475, 1578 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.85 (t, J=7.4 Hz, 3H), 1.51–1.64 (m, 2H), 1.87–1.94 (m, 2H), 4.49 (t, J=6.6 Hz, 1H), 7.24–7.30 (m, 6H), 7.56–7.59 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.2, 21.4, 43.7, 47.9, 127.8 (2C), 128.8 (4C), 130.2 (2C), 134.5 (4C). Anal. Calcd for $C_{16}H_{18}Se_2$: C, 52.19; H, 4.93. Found: C, 51.97; H, 4.78.

4.1.3. 1,1-Diphenylseleno decane (entry 3, Table 1)

A yellow liquid; IR (neat): 1436, 1475, 1578 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, J=6.5 Hz, 3H), 1.21–1.29 (m, 11H), 1.52–1.61 (m, 3H), 1.88–1.96 (m, 2H), 4.48 (t, J=6.5 Hz, 1H), 7.25–7.29 (m, 6H), 7.56–7.59 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1, 22.6, 28.3, 28.8, 29.2, 29.3, 29.4, 31.8, 37.0, 44.1, 127.9 (2C), 128.9 (4C), 130.4

(2C), 134.6 (4C). Anal. Calcd for $C_{22}H_{30}Se_2$: C, 58.41; H, 6.68. Found: C, 58.25; H, 6.53.

4.1.4. 1,1-Diphenylseleno tetradecane (entry 4, Table 1)

A pale yellow viscous oil; IR (neat): 1437, 1475, 1578 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, J=6.4 Hz, 3H), 1.06–1.35 (m, 19H), 1.51–1.56 (m, 3H), 1.88–1.95 (m, 2H), 4.47 (t, J=6.7 Hz, 1H), 7.22–7.29 (m, 6H), 7.56–7.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.0, 22.5, 28.1, 28.7, 29.2 (2C), 29.3, 29.4, 29.5 (2C), 29.54, 31.8, 36.9, 44.0, 127.8 (2C), 128.8 (4C), 130.3 (2C), 134.5 (4C). Anal. Calcd for $C_{26}H_{38}Se_2$: C, 61.41; H, 7.53. Found: C, 61.23; H, 7.42.

4.1.5. 3-Phenyl-1,1-diphenylseleno propane (entry 5, Table 1)

A pale yellow liquid; IR (neat): 1438, 1477, 1577 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.13–2.20 (m, 2H), 2.81 (t, J=7.5 Hz, 2H), 4.34 (t, J=6.6 Hz, 1H), 6.96–6.98 (m, 2H), 7.10–7.22 (m, 9H), 7.46–7.49 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 34.8, 38.9, 43.0, 126.5, 128.4 (2C), 128.9 (2C), 129.0 (2C), 129.5 (4C), 130.8, 135.2 (4C), 141.0 (2C). Anal. Calcd for $C_{21}H_{20}Se_2$: C, 58.62; H, 4.68. Found: C, 58.38; H, 4.54.

4.1.6. 1-Cyclohexyl-1,1-diphenylseleno methane (entry 6, Table 1)

A pale yellow liquid; IR (neat): 1437, 1475, 1577 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.15–1.26 (m, 2H), 1.31–1.42 (m, 4H), 1.62–1.78 (m, 4H), 1.88–1.92 (m, 1H), 4.44 (d, J=3.1 Hz, 1H), 7.20–7.29 (m, 6H), 7.48–7.53 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 26.1 (3C), 31.2 (2C), 43.9, 54.7, 127.7 (2C), 129.0 (4C), 131.4 (2C), 134.3 (4C). Anal. Calcd for $C_{19}H_{22}Se_2$: C, 55.89; H, 5.43. Found: C, 55.69; H, 5.31.

4.1.7. 2-Methyl-1,1-diphenylseleno propane (entry 7, Table 1)

A yellow liquid; IR (neat): 1437, 1475, 1578 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.02 (d, J=6.7 Hz, 6H), 2.09–2.15 (m, 1H), 4.48 (d, J=2.9 Hz, 1H), 7.23–7.28 (m, 6H), 7.53–7.56 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.3 (2C), 33.6, 55.7, 127.6 (2C), 128.9 (4C), 131.1 (2C), 134.2 (4C). Anal. Calcd for $C_{16}H_{18}Se_2$: C, 52.19; H, 4.93. Found: C, 51.95; H, 4.76.

4.1.8. (4-Thiomethylphenyl)methyl phenyl selenide (entry 9, Table 1)

A yellow solid; mp 55–57 °C; IR (KBr): 1438, 1475, 1577 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.44 (s, 3H), 4.06 (s, 2H), 7.08–7.24 (m, 7H), 7.41–7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.6, 31.7, 126.6 (2C), 127.2, 128.3, 128.8 (2C), 129.2 (2C), 130.2, 133.5 (2C), 135.4. Anal. Calcd for $C_{14}H_{14}Se$: C, 57.33; H, 4.81. Found: C, 57.05; H, 4.63.

4.1.9. (4-Allyloxy-3-methoxyphenyl)methyl phenyl selenide (entry 10, Table 1)

A yellow gummy liquid; IR (neat): 1263, 1436, 1475, 1510, 1577 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.76 (s, 3H), 4.06 (s, 2H), 4.54–4.58 (m, 2H), 5.25–5.42 (m, 2H), 6.01–6.07 (m, 1H), 6.66–6.76 (m, 3H), 7.19–7.25 (m, 3H), 7.42–7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 32.5, 55.9, 69.9, 112.3, 113.2, 117.9, 120.8, 122.6, 127.3, 128.9 (2C), 130.3, 133.3, 133.8 (2C), 146.9, 149.1. Anal. Calcd for $C_{17}H_{18}O_2Se$: C, 61.26; H, 5.44. Found: C, 61.06; H, 5.30.

4.1.10. (4-N,N-Dimethylphenyl)methyl phenyl selenide (entry 11, Table 1)

A yellow solid; mp 62–65 °C; IR (KBr): 1438, 1485, 1500, 1577 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.91 (s, 6H), 4.09 (s, 2H), 6.60–6.65 (m, 2H), 7.10–7.13 (m, 2H), 7.22–7.25 (m, 3H), 7.45–7.48 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.9, 40.5 (2C), 112.5 (2C), 125.8, 126.8, 128.7 (2C), 129.5 (2C), 131.1, 132.9 (2C), 149.4. Anal. Calcd for $C_{15}H_{17}NSe$: C, 62.07; H, 5.90. Found: C, 61.85; H, 5.73.

4.1.11. (4-Acetylphenyl)methyl phenyl selenide (entry 12, Table 1)

A pale yellow oil; IR (neat): 1436, 1475, 1577, 1762 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.27 (s, 3H), 4.08 (s, 2H), 6.95 (d, J=8.4 Hz, 2H), 7.16–7.25 (m, 5H), 7.41–7.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.9, 30.9, 121.3 (2C), 127.3, 128.9 (2C), 129.7 (2C), 129.9, 133.6 (2C), 136.1, 149.3, 169.3. Anal. Calcd for $C_{15}H_{14}O_2Se$: C, 59.02; H, 4.62. Found: C, 58.78; H, 4.43.

4.1.12. (2-Methoxyphenyl)methyl phenyl selenide (entry 13, Table 1)

A yellow liquid; IR (neat): 1247, 1437, 1475, 1577 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.79 (s, 3H), 4.12 (s, 2H), 6.78–6.84 (m, 2H), 7.02–7.04 (m, 1H), 7.16–7.25 (m, 4H), 7.45–7.49 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 26.7, 55.2, 110.4, 120.1, 126.9, 127.6, 128.1, 128.6 (2C), 129.9, 131.4, 133.6 (2C), 156.9. Anal. Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.40; H, 4.88.

4.1.13. (3-Methoxyphenyl)methyl phenyl selenide (entry 14, Table 1)

A yellow gummy oil; IR (neat): 1263, 1436, 1475, 1583 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.66 (s, 3H), 4.00 (s, 2H), 6.64–6.74 (m, 3H), 7.06–7.11 (m, 1H), 7.15–7.19 (m, 3H), 7.37–7.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 32.1, 54.9, 112.6, 113.9, 121.0, 127.2, 128.8 (2C), 129.3, 130.3, 133.5 (2C), 140.0, 159.4. Anal. Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.42; H, 4.93.

4.1.14. (4-Methoxyphenyl)methyl phenyl selenide (entry 15, Table 1)

A yellow gummy liquid; IR (neat): 1438, 1475, 1577 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.77 (s, 3H), 4.08 (s, 2H), 6.78 (d, J=8.7 Hz, 2H), 7.12 (d, J=8.7 Hz, 2H), 7.23–7.26 (m, 3H), 7.43–7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.6, 55.1, 113.7 (2C), 127.0, 128.8 (2C), 129.8 (2C), 130.4, 131.4, 133.3 (2C), 158.4. Anal. Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.41; H, 4.88.

4.1.15. 3-Bromophenyl-1-selenophenylmethane (entry 17, Table 1, major)

A yellow oil; IR (neat): 1437, 1475, 1577 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 4.00 (s, 2H), 7.06–7.08 (m, 2H), 7.23–7.30 (m, 5H), 7.40–7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.9, 122.7, 127.8, 128.1, 129.5 (2C), 130.1, 130.3 (2C), 132.2, 134.4 (2C), 141.5. Anal. Calcd for $C_{13}H_{11}BrSe$: C, 47.88; H, 3.40. Found: C, 47.63; H, 3.25.

4.1.16. 3-Bromophenyl-1,1-diselenophenylmethane (entry 17, Table 1, minor)

A yellow gummy liquid; IR (neat): 1436, 1473, 1576 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 5.39 (s, 1H), 7.00–7.06 (m, 1H), 7.14–7.33 (m, 8H), 7.35 (s, 1H), 7.40–7.43 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 42.4, 121.9, 126.5, 128.2 (2C), 128.9 (4C), 129.6, 130.2, 130.3 (2C), 130.9, 134.7 (4C), 143.4. Anal. Calcd for $C_{19}H_{15}BrSe_2$: C, 47.43; H, 3.14. Found: C, 47.19; H, 2.98.

4.1.17. 1-(Bis(phenylselanyl)methyl)-4-fluorobenzene (entry 19, Table 1, major)

A light-yellow liquid; IR (neat): 686, 734, 835, 1020, 1064, 1157, 1228, 1296, 1434, 1473, 1508, 1573, 1600, 1681, 2852, 2923, 2995, 3055 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 5.50 (s, 1H), 6.87–6.92 (m, 2H), 7.21–7.30 (m, 8H), 7.43–7.46 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 42.6, 115.2 (d, J_{C-F}=21.6 Hz, 2C), 128.4 (2C), 129.1 (4C), 129.8 (d, J_{C-F}=8.3 Hz, 2C), 130.8 (2C), 134.8 (4C), 137.2, 161.9 (d, J_{C-F}=245.1 Hz). Anal. Calcd for $C_{19}H_{15}FSe_2$: C, 54.30; H, 3.60. Found: C, 54.24; H, 3.57.

4.1.18. (4-Fluorobenzyl)(phenyl)selane (entry 19, Table 1, minor)

A light-yellow liquid; IR (neat): 690, 736, 835, 1157, 1226, 1506, 1579, 1600, 2929, 2999, 3053 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.99 (s, 2H), 6.81–6.87 (m, 2H), 7.04–7.08 (m, 2H), 7.16–7.18 (m, 3H), 7.34–7.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.4, 115.3

(d, J_{C-F}=21.5 Hz, 2C), 127.5, 129.1 (2C), 130.4 (d, J_{C-F}=8.0 Hz, 2C), 130.6, 133.9 (2C), 134.5, 161.8 (d, J_{C-F}=244.0 Hz). Anal. Calcd for $C_{13}H_{11}FSe$: C, 58.88; H, 4.18. Found: C, 58.90; H, 4.15.

4.1.19. 4-(Phenylselanylmethyl)phenyl 4-methyl benzenesulfonate (entry 21, Table 1)

A yellowish solid; mp 108–110 °C; IR (KBr): 553, 657, 688, 711, 732, 813, 866, 1151, 1176, 1199, 1377, 1500, 1595, 1703, 2916, 3043 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.37 (s, 3H), 3.94 (s, 2H), 6.76 (d, J=8.5 Hz, 2H), 6.99 (d, J=8.5 Hz, 2H), 7.14–7.23 (m, 5H), 7.31 (d, J=7.8 Hz, 2H), 7.60 (d, J=8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.8, 31.4, 122.3 (2C), 127.7 (2C), 128.6 (2C), 129.0 (2C), 129.6, 129.8 (2C), 130.0 (2C), 132.4, 134.0, 137.9, 145.4, 148.4. Anal. Calcd for $C_{20}H_{18}O_3SSe$: C, 57.55; H, 4.35. Found: C, 57.51; H, 4.33.

4.1.20. General experimental procedure for dithioacetalization. Representative one for 4-chlorobenzaldehyde (entry 4, Table 2)

To a stirred mixture of 4-chlorobenzaldehyde (141 mg, 1 mmol), dimethyl disulfide (170 mg, 1.8 mmol) and indium metal (115 mg, 1 mmol, cut into small pieces) in dry acetonitrile (2.5 mL) was added trimethylchlorosilane (327 mg, 3 mmol) and the mixture was stirred at room temperature for 2 min followed by heating under reflux for 2 h (as monitored by TLC). Acetonitrile was evaporated under reduced pressure and the residue was extracted with ether (3×10 mL). The ether extract was washed with water and dried (Na_2SO_4). Evaporation of solvent left the crude product, which was purified by column chromatography over silica gel using hexane–ether (98:2) as eluant to afford a pure dimethylthioacetal of 4-chlorobenzaldehyde as a colourless oil (157 mg, 72%). The spectroscopic data (IR, ^1H and ^{13}C NMR) of this compound are in good agreement with those reported.[15]

This procedure was followed for all the reactions listed in Table 2. Most of these compounds (entries 1–4, 7, 10–14, Table 2) are known and were identified by comparison of their spectroscopic data with those reported (references in Table 2). The unknown compounds (entries 5, 6, 8, 9, Table 2) were characterized by their spectroscopic data (IR, ^1H and ^{13}C NMR) and elemental analysis. These data are given below.

4.1.21. 4-(Bis(methylthio)methyl)phenyl acetate (entry 5, Table 2)

A yellowish liquid; IR (neat): 651, 763, 858, 912, 1016, 1164, 1199, 1369, 1504, 1766, 2916 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.12 (s, 6H), 2.31 (s, 3H), 4.80 (s, 1H), 7.08 (d, J=8.49 Hz, 2H), 7.45 (d, J=8.52 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.1 (2C), 21.3, 55.9, 121.6 (2C), 128.8 (2C), 137.3, 150.2, 169.4. Anal. Calcd for $C_{11}H_{14}O_2S_2$: C, 54.51; H, 5.82. Found: C, 54.41; H, 5.89.

4.1.22. 4-(Bis(methylthio)methyl)phenyl 4-methyl benzenesulfonate (entry 6, Table 2)

A yellowish liquid; IR (neat): 659, 711, 813, 837, 866, 1093, 1153, 1176, 1197, 1373, 1498, 1596, 2916, 2979 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.03 (s, 6H), 2.41 (s, 3H), 4.72 (s, 1H), 6.93 (d, J=8.62 Hz, 2H), 7.28 (d, J=8.40 Hz, 2H), 7.31 (d, J=8.62 Hz, 2H), 7.67 (d, J=8.16 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.9 (2C), 21.7, 55.7, 122.4 (2C), 128.5 (2C), 128.9 (2C), 129.8 (2C), 132.3, 138.8, 145.5, 148.9. Anal. Calcd for $C_{16}H_{18}O_3S_3$: C, 54.21; H, 5.12. Found: C, 54.17; H, 5.09.

4.1.23. 1-(Bis-methyl sulfanyl-methyl)-4-fluorobenzene (entry 8, Table 2)

A colourless liquid; IR (neat): 843, 1157, 1223, 1506, 1601, 2916, 2979 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.00 (s, 6H), 4.68 (s, 1H), 6.90–6.96 (m, 2H), 7.29–7.34 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.0 (2C), 55.8, 115.4 (d, J_{C-F}=21.8 Hz, 2C), 129.3 (d, J_{C-F}=8.2 Hz, 2C), 135.6, 162.2 (d, J_{C-F}=245.3 Hz). Anal. Calcd for $C_9H_{11}FS_2$: C, 53.43; H, 5.48. Found: C, 53.46, H, 5.45.

4.1.24. 2-(Bis(methylthio)methyl)-1,3-dichlorobenzene (entry 9, Table 2)

A light-yellow liquid; IR (neat): 696, 777, 1087, 1175, 1435, 1456, 1558, 1577, 2914, 2976, 3065 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.14 (s, 6H), 5.41 (s, 1H), 7.00–7.02 (m, 1H), 7.17–7.21 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 17.8 (2C), 54.0, 127.9, 128.9, 130.6, 133.6, 135.9, 136.0. Anal. Calcd for $C_9H_{10}Cl_2S_2$: C, 42.69; H, 3.98. Found: C, 42.67; H, 3.99.

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