On the reactivity of indium(III) benzenechalcogenolates (chalcogen = sulfur and selenium) towards organyl halides for the synthesis of organyl phenyl chalcogenides

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Abstract: The reactivity of indium(III) benzenechalcogenolates (chalcogen = sulfur, selenium) towards organyl halides (organyl = alkyl, allyl, benzyl, acyl) was examined. A practical one-pot method to prepare organyl phenyl chalcogenides from indium metal and diphenyl dichalcogenide was found. The coupling is fairly broad in scope and generally works better for organyl halides capable to produce stable carbocations.

Key words: diphenyl diselenide, diphenyl disulfide, indium(III) benzenechalcogenolates, organyl phenyl chalcogenides.

Résumé : On a étudié la réactivité des benzènechalcogénolates d'indium(III) (chalcogène = soufre, sélénium) vis-à-vis des halogénures d'organyles (organyle = alkyle, allyle, benzyle, acyle). On a mis au point une méthode monotope pratique de préparer des chalcogénures d'organyle et de phényle à partir de l'indium métallique et du dichalcogénure de diphényle. La portée de la réaction de couplage est assez large et elle fonctionne généralement mieux avec les halogénures d'organyle susceptibles de donner naissance à des carbocations stables.

Mots-clés : diséléniure de diphényle, disulfure de diphényle, benzènechalcogénolates d'indium(III), chalcogénures d'organyle et de phényle.

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Introduction

Indium(III) arylchalcogenolates, $In(EAr)_3$ (E = S, Se), were prepared by methathetical reactions,[1,2] redox processes,[3,4] and electrochemically by sacrificing indium electrodes.[5] Heteroleptic compounds bearing a halide ligand, $XIn(EPh)_2$ (X = Cl, Br, I; E = S, Se), were prepared by the oxidative insertion of the corresponding indium monohalide into the dichalcogenides.[6] $In(SePh)_3$ was found polymeric by X-ray means, crystallizing in two polymorfic forms: a triclinic containing five-coordinated indium centers with asymmetrical bridging benzeneselenolate ligands[7] and a monoclinic containing six-coordinated indium atoms with symmetrical bridging benzeneselenolate ligands.[8] The sulfur analogue, $In(SPh)_3$, is also believed to be polymeric,[2] but its X-ray structure was not established until now. However, the sterically hindered arylthiolate complex $(2,4,6\text{-}t\text{-}Bu_3C_6H_2S)_3In$, soluble in organic solvents, was crystallized and had its distorted trigonal planar structure determined by X-ray methods.[9] A common property relating both the homoleptic $In(EPh)_3$ and the heteroleptic $XIn(EPh)_2$ compounds is that they act as Lewis acids, forming stable molecular adducts with several nitrogen,[1–3,6,8] phosphorus,[1,3,4] sulfoxide,[1] and halide[1,3] ligands.

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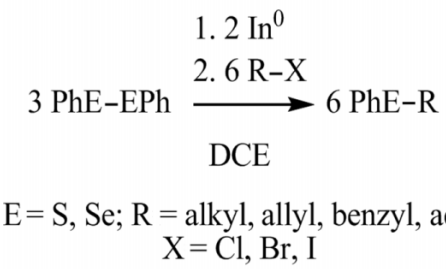
Indium(III) chalcogenolates contain indium–chalcogen bonds made of a hard In(III) cation[10] and a soft thiolate and (or) selenolate anions.[11,12] Hard acids – soft bases complexes possess intrinsic thermodynamic unstability, suggesting that the chalcogenolate anion could effectively be used as a nucleophile in organic reactions to produce new carbon–chalcogen bonds. Our group and other groups have introduced the heteroleptic $XIn(EPh)_2$ compounds as sources of the benzenechalcogenolate nucleophiles to produce organic chemicals of interest in reactions, such as ring opening of epoxides to β–hydroxyselenides[13] and sulfides,[14] ring opening of aziridines to selenocysteine and selenotreonine,[15] hydrochalcogenation of alkynes[16–18] to vinyl chalcogenides, also obtained through Pd(0)-catalyzed coupling of $IIn(SePh)_2$ with vinyl bromides[19], and finally for coupling with organyl halides to organyl phenyl chalcogenides.[20,21]

Recently, while trying to hydrochalcogenate aminoalkines with the heteroleptic compounds, $XIn(EPh)_2$, we observed ineffectiveness.[22] The task was accomplished with the indium(III) benzenechalcogenolate complexes, $In(EPh)_3$ (E = S, Se) generated by refluxing a 2:3 molar ratio of the metallic element and the corresponding diphenyl dichalcogenide in dichloroethane (DCE). The cleavage of the chalcogen–chalcogen bond by indium metal in mild conditions to the $In(EPh)_3$ compounds capable to deliver the benzenechalcogenolate nucleophiles is very attractive to the synthetic chemist because of the nontoxic nature and the stability of indium towards air and moisture. Furthermore, to replace the air-sensitive indium(I) halides to promote the cleavage of the chalcogen–chalcogen bonds is also desirable because it will allow to conduct one-pot

preparations directly from the stable metal. To gain a better understanding on the reactivity pattern of the $In(EPh)_3$ compounds generated by this method, we have examined their reactions with organyl halides (Scheme 1). We also compared the new results with the ones obtained using earlier similar procedures leading to PhER compounds involving the cleavage of the dichalcogenides by InI[20,21] and In metal.[23] A striking difference in reactivity, depending on the organyl halides, was observed; this was interpreted in terms of the polymeric nature of the $In(EPh)_3$ compounds and allowed to design experiments to the chemoselective production of a desired PhER compound.

Scheme 1. One-pot preparation of organyl phenyl chalcogenides.



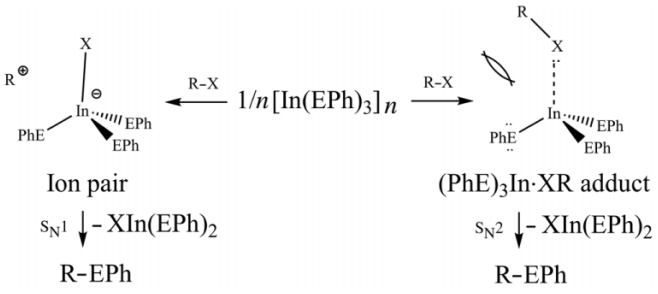
Results and discussion

The $In(EPh)_3$ (E = S, Se) compounds were easily prepared by refluxing 2:3 molar quantities of elemental indium and the dichalcogenide in DCE. Typically, the metal was consumed after 1–2 h, but sonication of a suspension of the metal in DCE for 10 min prior to heating accelerated the process. The selenium product remained in solution, while the sulfur analogue precipitated as a white powder. Addition of 3 equiv. of the organyl halides depicted in Table 1 afforded the corresponding organyl phenyl chalcogenides products with condensation of up to three benzenechalcogenolate ligands from the $In(EPh)_3$ reagents. The nucleophilic substitution is easily followed by TLC chromatography, and in the case of the sulfur complex, reaction completeness is verified just by observing the dissolution of the reagent in the reaction media; in most cases, optimum yields were obtained as soon as the white precipitate dissolved.

The reactivity trends of the organyl halides in condensations with the benzenechalcogenolate nucleophiles from the $IIn(EPh)_2$ (E = S, Se) compounds in dichloromethane was investigated by Ranu and co-workers, who demonstrated that primary, secondary, benzylic, and allylic chlorides, bromides, and iodides as well as acid chlorides readily participated in the reaction to form the desired organyl phenyl chalcogenides.[20,21] Jang and co-workers examined the problem through a one-pot reaction involving metallic indium, diphenyl diselenide, and organyl halides; in that work, they found that the reaction is initiated by organyl radicals generated by a one-electron reduction of the R–X substrate by metallic indium. Accordingly, a relative I > Br > Cl reactivity order was established for the organyl halides.[23]

There are remarkable differences in the reactivity of the $In(EPh)_3$ compounds towards organyl halides compared with the reagents discussed above. In the present work, we have verified that the nature of the organyl moiety of the halide controls the efficiency of the process. Tertiary, benzylic, allylic (leading exclusively to the α-coupling product), and acyl halides (Table 1, entries 22–39) instantaneously reacted with the $In(EPh)_3$ compounds at room temperature to produce good yields of the desired product. Reactions involving primary halides (Table 1, entries 1–17 and 40–42), on the other hand, took several hours for completion even with heating at 83 °C or completely resisted the transformation as observed for the chlorides (Table 1, entries 1 and 2). We further note that only the higher members of the series of bis(phenyl chalcogen)alkanes $PhE(CH_2)_nEPh$ (n = 1, 2, 3, 5, or 10) were efficiently obtained from the corresponding

Scheme 2. Proposed pathway for reaction of $In(EPh)_3$ and RX.



dibromo substrates (Table 1, entries 9–17). Secondary alkyl halides (Table 1, entries 18–21) failed to undergo efficient condensations, and surprisingly, from these reactions with $In(SePh)_3$ (Table 1, entries 19 and 21), we have isolated 1,4-bis(phenyl selanyl)butane, $PhSe(CH_2)_4SePh$ (0.83 mmol per 1 mmol of $In(SePh)_3$), fully characterized by elemental analysis, mass spectrometry, and ^1H and ^{13}C NMR spectroscopy; the actual course of the reaction leading to the butane derivative is still undetermined, but it is important to notice that we did not observe any direct reaction between $In(SePh)_3$ and the DCE solvent under these experimental conditions, except perhaps in these two cases for which it is reasonable to assume solvent participation in the process.

The experimental observations made above seem to indicate that the polymeric nature of the $In(EPh)_3$ compounds is an important aspect ruling their reactivity pattern towards organyl halides, and that allows one to understand the differences when compared with reactions involving the $IIn(EPh)_2$ compounds[20,21] and the proposed free-radical process initiated by metallic indium.[23] The polymeric nature involving bridging benzenechalcogenolate ligands together with the ability of the $In(EPh)_3$ complexes to act as Lewis acids strongly suggest that depolymerization to reactive monomeric intermediates is achieved by halide coordination to the indium centers replacing the bridging chalcogenolate ligands responsible for holding the polymeric structures. Thus, it is expected that organyl halides capable to produce stable tertiary, benzylic, allylic, and acyl carbocations would be the most reactive substrates and that these will react according to an S_N1 path, possibly through an ion-pair intermediate. The instantaneous reactions at room temperature involving these substrates together with the deep colouration, typical of carbocations, developed in the DCE solutions particularly in reactions with benzylic and allylic halides, are in agreement with this picture (Scheme 2). The enormous difference in reactivity presented by primary alkyl

Table 1. One-pot preparation of organyl phenyl chalcogenides.

Entry	R–X	E	*T* (°C)	Time	Yield (%)[a]	Reference
1	*n*-$C_6H_{13}Cl$	S	83	20 h	NR[b]	—
2	*n*-$C_6H_{13}Cl$	Se	83	20 h	NR	—
3	*n*-C_4H_9Br	S	83	20 h	65	24
4	*n*-C_4H_9Br	Se	83	12 h	54	25
5	*n*-C_4H_9I	S	83	20 h	56	24
6	*n*-C_4H_9I	Se	83	12 h	55	—
7	*n*-$C_8H_{17}Br$	S	83	20 h	83	26
8	*n*-$C_8H_{17}Br$	Se	83	6 h	78	27
9	$Br(CH_2)_{10}Br$	S	83	16 h	80	28
10	$Br(CH_2)_{10}Br$	Se	83	6 h	80	—
11	$Br(CH_2)_5Br$	S	83	20 h	52	29
12	$Br(CH_2)_5Br$	Se	83	6 h	57	30
13	$I(CH_2)_3I$	S	83	48 h	NR	—
14	$I(CH_2)_3I$	Se	83	18 h	60	31
15	$Br(CH_2)_2Br$	S	83	48 h	NR	—
16	$Br(CH_2)_2Br$	Se	83	48 h	NR	—
17	CH_2I_2	S	83	48 h	NR	—
18	$CH_3CH(Br)C_2H_5$	S	83	24 h	Traces	—
19	$CH_3CH(Br)C_2H_5$	Se	83	6 h	25[c]	27
20	$C_6H_{11}Br$[d]	S	83	20 h	Traces	—
21	$C_6H_{11}Br$[d]	Se	83	18 h	Traces[c]	—
22	$(CH_3)_3CBr$	S	25	3 min	44	20
23	$(CH_3)_3CBr$	Se	25	3 min	68	27
24	$PhCH_2Br$	S	25	3 min	90	26
25	$PhCH_2Br$	Se	25	3 min	87	27
26	$PhCH(CH_3)Br$	S	25	3 min	95	32
27	$PhCH(CH_3)Br$	Se	25	3 min	87	20
28	$H_2C{=}CHCH_2Br$	S	25	3 min	75	26
29	$H_2C{=}CHCH_2Br$	Se	25	3 min	80	33
30	(*Z*+*E*)-$CH_3HC{=}CHCH_2Br$	S	25	3 min	66	20
31	(*Z*+*E*)-$CH_3HC{=}CHCH_2Br$	Se	25	3 min	94	33
32	(*E*)-$PhHC{=}CHCH_2Br$	S	25	3 min	54	20
33	(*E*)-$PhHC{=}CHCH_2Br$	Se	25	3 min	48	20
34	$H_2C{=}C(CH_3)CH_2Br$	S	25	3 min	73	26
35	$H_2C{=}C(CH_3)CH_2Br$	Se	25	3 min	88	—
36	CH_3COCl	S	25	3 min	66	34
37	CH_3COCl	Se	25	3 min	62	20
38	PhCOCl	S	25	3 min	89	34
39	PhCOCl	Se	25	3 min	87	33
40	$C_2H_5OC(O)CH_2Br$	S	83	24 h	50	20
41	$C_2H_5OC(O)CH_2Br$	Se	83	24 h	80	20
42	$PhC(O)CH_2Br$	S	83	24 h	78	26

[a]Isolated yield of analytically pure product.
[b]NR = No reaction.
[c]Plus 0.83 mmol of $PhSeCH_2(CH_2)_2CH_2SePh$ per 1.00 mmol of indium.
[d]Cyclohexyl bromide.

halides, which only reacted after prolonged refluxing in DCE (83 °C), and the lack of reactivity of secondary alkyl halides suggest an alternative pathway. We propose for these cases that depolymerization to reactive monomeric intermediates is achieved by formation of $(PhE)_3In{\cdot}X{-}R$ adducts by coordination of the halogen atom of the organyl halide to the indium centers. This description accommodates well the failure of secondary alkyl halides to react efficiently due to stereo-hindrance during adduct formation (Scheme 2). Together with the product of the coupling between the first equivalent of the phenyl chalcogenolate nucleophile with the organyl halide leading to the first equivalent of the non-symmetric PhE–R chalcogenide, occurs the simultaneous production of the indium(III) heteroleptic product $XIn(EPh)_2$ used by Ranu and co-workers in their earlier work,[20,21] a compound responsible for formation of the two extra equivalents of the PhE–R final product. Considering these ideas, one can understand the higher reactivity of the $IIn(EPh)_2$ compared with the indium(III) benzenechalcogenolate reagents with primary and secondary alkyl halides in terms of the degree of polymerization of the $XIn(EPh)_2$ and the $In(EPh)_3$ reagents. Although $In(EPh)_3$ are polymeric, there

must not be significant association of the $XIn(EPh)_2$ compounds in solutions.

The milder reactivity of the $In(EPh)_3$, compared with the $XIn(EPh)_2$ reagents[20,21] and with the radical species generated from the in situ reaction involving indium metal and diphenyl diselenide,[23] suggests that the indium(III) benzenechalcogenolates can chemoselectively produce R–EPh (R = ^{t}alkyl, allyl, or benzyl) in the presence of primary or secondary alkyl halides. Accordingly, a competitive experiment involving $In(SePh)_3$ with 3 mol of allyl bromide and *n*-bromobutane produced C_3H_5–SePh exclusively with no signs of ^{n}Bu–SePh being detected.

Conclusion

The development of a one-pot efficient synthesis of organyl phenyl chalcogenides from alkyl halides and diphenyl dichalcogenides with the cleavage of the chalcogen–chalcogen bond performed by metallic indium is very attractive to the synthetic chemists because of the easy handling and accentuated stability of the metallic element towards moisture and air. We have interpreted this process as being intermediated by $[In(EPh)_3]_n$ polymers whose association must be broken to monomeric complexes by coordination and (or) interaction with the halide atom of the organyl halide. The degree of this coordination or interaction determines the reactivity of these reagents towards the organyl halide. Organyl halides, giving stable carbocations, react promptly following an S_N1-type reaction pathway leading to high yields of the nonsymmetrical chalcogenides, while primary alkyl halides require long periods of continuous heating, possibly following an S_N2-type process. The striking difference in reactivity, depending on the nature of the organyl halide, allows selective condensations as we have demonstrated with the experiment involving allyl bromide and bromobutane, which produced exclusively the allyl selenide.

Experimental

General

Indium powder and diphenyl disulfide were commercial products from Aldrich. Diphenyl diselenide was prepared from phenylmagnesium bromide and elemental selenium.[35] DCE was dried over CaH_2 and distilled before use. All the organyl halides were obtained from commercial suppliers and distilled, when necessary, before use. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker DPX 200 and (or) Bruker DPX 400 spectrometers.

Preparation of organyl phenyl chalcogenides

To a Schlenk tube truly dried (flame) was sequentially added DCE (2 mL), diphenyl dichalcogenide (0.52 mmol), and indium powder (0.35 mmol). The mixture was sonicated for 10 min and then heated under reflux for 1–2 h. After all the metal being consumed, a yellow solution is obtained for the selenium derivative and a white precipitate for the sulfur case. At this point, the reaction was brought to room temperature, and the organyl halide (1 mmol) was added. The substrates corresponding to entries 22–39 (Table 1) were immediately (1–3 min) consumed as verified by TLC, while the remaining were consumed after heating for the periods specified in Table 1. The reactions were quenched with distilled water (10 mL), the organics extracted with dichloromethane (3 × 10 mL), the extracts were sequentially dried over sodium sulfate, evaporated to dryness (vaccum), and the organyl phenyl chalcogenides purified by column chromatography over silica gel using hexanes/ ethyl acetate mixtures. The sulfur derivatives are colourless oils or solids, while the selenium products are yellow compounds. All products are known compounds, and they were identified by comparison of their spectral data (^{1}H and ^{13}C NMR) with those reported in the literature (see Table 1 for references).

n-*Butyl phenyl sulfide (Table 1, entries 3 and 5)*

^{1}H NMR ($CDCl_3$) δ: 7.25–7.04 (m, 5H), 2.81 (t, *J* = 7.5 Hz, 2H), 1.53 (qui, *J* = 7.5 Hz, 2H), 1.34 (sex, *J* = 7.5 Hz, 2H), 0.81 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 136.96, 128.70, 128.67, 125.48, 33.10, 31.11, 21.87, 13.57.

n-*Butyl phenyl selenide (Table 1, entries 4 and 6)*

^{1}H NMR ($CDCl_3$) δ: 7.42–7.38 (m, 2H), 7.18–7.10 (m, 3H), 2.83 (t, *J* = 7.6 Hz, 2H), 1.61 (qui, *J* = 7.6 Hz, 2H), 1.34 (sex, *J* = 7.6 Hz, 2 H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 132.29, 130.66, 128.90, 126.50, 32.19, 27.55, 22.89, 13.50.

n-*Octyl phenyl sulfide (Table 1, entry 7)*

^{1}H NMR ($CDCl_3$) δ: 7.28–7.04 (m, 5H), 2.84 (t, *J* = 7.5 Hz, 2H), 1.58 (qui, *J* = 7.5 Hz, 2H), 1.32–1.16 (broad, 10H), 0.82 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 137.04, 128.94, 128.68, 125.46, 33.44, 31.73, 29.10, 29.06, 28.78, 22.58, 14.03.

n-*Octyl phenyl selenide (Table 1, entry 8)*

^{1}H NMR ($CDCl_3$) δ: 7.44–7.39 (m, 2H), 7.20–7.12 (m, 3H), 2.84 (t, *J* = 7.3 Hz, 2H), 1.64 (qui, *J* = 7.3 Hz, 2H), 1.33–1.16 (broad, 10H), 0.82 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 132.28, 130.70, 128.86, 126.46, 31.74, 30.09, 29.78, 29.11, 28.99, 27.87, 22.58, 14.03.

1,10-Bis(phenylthio)decane (Table 1, entry 9)

Mp 64–65 °C. ^{1}H NMR ($CDCl_3$) δ: 7.25–7.10 (m, 10H), 2.82 (t, *J* = 7.4 Hz, 4H), 1.56 (qui, *J* = 7.3 Hz, 4H), 1.36–1.15 (broad, 12H). ^{13}C NMR ($CDCl_3$) δ: 136.98, 128.97, 128.73, 125.53, 33.46, 33.28, 29.31, 29.04, 28.72.

1,10-Bis(phenyl selanyl)decane (Table 1, entry 10)

Mp 67–68 °C. ^{1}H NMR ($CDCl_3$) δ: 7.41–7.35 (m, 4H), 7.18–7.10 (m, 6H), 2.81 (t, *J* = 7.4 Hz, 4H), 1.60 (qui, *J* = 7.2 Hz, 4H), 1.32–1.14 (broad, 12H). ^{13}C NMR ($CDCl_3$) δ: 132.23, 130.63, 128.86, 126.46, 30.03, 29.70, 29.30, 28.94, 27.81.

1,5-Bis(phenylthio)pentane 7 (Table 1, entry 11)

^{1}H NMR ($CDCl_3$) δ: 7.24–7.06 (m, 10H), 2.80 (t, *J* = 6.9 Hz, 4H), 1.61–1.41(m, 6H). ^{13}C NMR ($CDCl_3$) δ: 136.62, 128.93, 128.77, 125.69, 33.33, 28.56, 27.78.

1,5-Bis(phenyl selanyl)pentane (Table 1, entry 12)

^{1}H NMR ($CDCl_3$) δ: 7.38–7.34 (m, 4H), 7.15–7.08 (m, 6H), 2.76 (t, *J* = 7.3 Hz, 4H), 1.58 (qui, *J* = 7.6 Hz, 4H), 1.40 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 132.34, 130.32, 128.86, 126.54, 29.72, 29.41, 27.49.

1,3-Bis(phenyl selanyl)propane (Table 1, entry 14)

^{1}H NMR ($CDCl_3$) δ: 7.38–7.34 (m, 4H), 7.16–7.11 (m, 6H), 2.89 (t, J = 7.3 Hz, 4H), 1.95 (qui, J = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 132.59, 129.81, 128.95, 126.77, 30.10, 27.34.

sec-*Butyl phenyl selenide (Table 1, entry 19)*

^{1}H NMR ($CDCl_3$) δ: 7.51–7.44 (m, 2H), 7.19–7.15 (m, 3H), 3.16 (sex, J = 6.8 Hz, 1H), 1.57 (m, 2H), 1.31 (d, J = 6.9 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 134.78, 129.12, 128.77, 127.18, 41.44, 30.37, 21.53, 12.25.

tert-*Butyl phenyl sulfide (Table 1, entry 22)*

^{1}H NMR ($CDCl_3$) δ: 7.48–7.41 (m, 2H), 7.28–7.19 (m, 3H), 1.22 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 137.47, 128.62, 128.41, 127.13, 45.82, 30.92.

tert-*Butyl phenyl selenide (Table 1, entry 23)*

^{1}H NMR ($CDCl_3$) δ: 7.59–7.53 (m, 2H), 7.29–7.17 (m, 3H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 138.11, 128.52, 128.36, 128.28, 43.00, 32.12.

Benzyl phenyl sulfide (Table 1, entry 24)

Mp 39–40 °C. ^{1}H NMR ($CDCl_3$) δ: 7.25–7.08 (m, 10H), 4.02 (s, 2H). ^{13}C NMR ($CDCl_3$) δ: 137.37, 136.32, 129.71, 128.76, 128.74, 128.41, 127.09, 126.24, 38.93.

Benzyl phenyl selenide (Table 1, entry 25)

Mp 32–33 °C. ^{1}H NMR ($CDCl_3$) δ: 7.35–7.31 (m, 2H), 7.14–7.05 (m, 8H), 3.98 (s, 2H). ^{13}C NMR ($CDCl_3$) δ: 138.48, 133.37, 130.33, 128.85, 128.72, 128.29, 127.14, 126.73, 32.07.

1-Phenylethyl phenyl sulfide (Table 1, entry 26)

^{1}H NMR ($CDCl_3$) δ: 7.29–7.15 (m, 10H), 4.32 (q, J = 7.0 Hz, 1H), 1.61 (d, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 143.14, 135.07, 132.40, 128.60, 128.31, 127.20, 127.05, 127.02, 47.91, 22.27.

1-Phenylethyl phenyl selenide (Table 1, entry 27)

^{1}H NMR ($CDCl_3$) δ: 7.44–7.38 (m, 2H), 7.23–7.12 (m, 8H), 4.42 (q, J = 7.0 Hz, 1H), 1.72 (d, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 143.48, 135.32, 129.76, 128.68, 128.19, 127.65, 127.12, 126.80, 42.33, 22.09.

Allyl phenyl sulfide (Table 1, entry 28)

^{1}H NMR ($CDCl_3$) δ: 7.27–7.07 (m, 5H), 5.79 (d of sex, J = 6.8 Hz, 3.0 Hz, 1H), 5.01 (m, 2H), 3.45 (d of t, J = 6.7 Hz, 0.9 Hz, 2H).

Allyl phenyl selenide (Table 1, entry 29)

^{1}H NMR ($CDCl_3$) δ: 7.51–7.46 (m, 2H), 7.28–7.20 (m, 3H), 5.94 (d of sex, J = 7.0 Hz, 2.3 Hz, 1H), 4.95 (m, 2H), 3.51 (d, J = 7.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 134.35, 133.31, 129.15, 128.91, 127.10, 116.81, 30.65.

Crotyl phenyl sulfide, mixture of isomers, cis:trans = 1:4 (Table 1, entry 30)

^{1}H NMR ($CDCl_3$) δ: 7.26–7.04 (m, 5H), 5.53–5.39 (m, 2H), 3.48–3.44 (m, 1.6H), 3.22–3.18 (m, 0.4H), 1.59 (t, J = 4.8 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 130.22, 129.55, 129.25, 129.05, 128.90, 128.70, 127.46, 127.13, 126.03, 126.03, 125.96, 125.92, 36.79, 36.34, 17.95, 17.73.

Crotyl phenyl selenide, mixture of isomers, cis:trans = 1:4 + traces of 3-benzenoselanyl-butene-1 (Table 1, entry 31)

^{1}H NMR ($CDCl_3$) δ: 7.52–7.41 (m, 2H), 7.24–7.20 (m, 3H), 5.67–5.31 (m, 2H), 3.55(d, J = 7.8 Hz, 0.4H), 3.48 (dd, J = 7.0 Hz, 1.1 Hz, 1.6H), 1.61 (dd, J = 6.0 Hz, 1.1 Hz, 2.4H), 1.47 (dd, J = 5.2 Hz, 1.3 Hz, 0.6H). ^{13}C NMR ($CDCl_3$) δ: 133.53, 133.15, 131.39, 130.31, 129.07, 128.76, 128.74, 128.22, 127.59, 127.00, 126.92, 126.88, 126.82, 126.01, 29.99, 24.29, 17.60, 12.27.

trans-*Cinnamyl phenyl sulfide (Table 1, entry 32)*

Mp 74–75 °C. ^{1}H NMR ($CDCl_3$) δ: 7.39–7.11 (m, 10H), 6.40 (d, J = 15.8 Hz, 1H), 6.21 (d of t, J = 15.8 Hz, 6.9 Hz, 1H), 3.67 (d, J = 6.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 136.59, 135.36, 132.65, 130.05, 128.75, 128.42, 127.47, 126.27, 126.23, 124.91, 36.93.

trans-*Cinnamyl phenyl selenide (Table 1, entry 33)*

Mp 61–62 °C. ^{1}H NMR ($CDCl_3$) δ: 7.45–7.37 (m, 2H), 7.18–7.09 (m, 8H), 6.30–6.07 (m, 2H), 3.57 (d, J = 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 136.72, 133.81, 131.97, 129.77, 128.87, 128.41, 127.34, 127.23, 126.17, 125.79, 30.63.

2-Methylallyl phenyl sulfide (Table 1, entry 34)

^{1}H NMR ($CDCl_3$) δ: 7.34–7.15 (m, 5H), 4.81 (dd, J = 0.7 Hz, 2H), 3.51 (s, 2H), 1.84 (d, J = 0.7 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 140.75, 136.40, 129.92, 128.66, 126.13, 113.90, 41.85, 21.09.

2-Methylallyl phenyl selenide (Table 1, entry 35)

^{1}H NMR ($CDCl_3$) δ: 7.42–7.38 (m, 2H), 7.18–7.13 (m, 3H), 4.63 (m, 1H), 4.61 (m, 1H), 3.42 (d, J = 0.8 Hz, 2H), 1.77 (dd, J = 0.8 Hz, 0.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 141.70, 133.42, 130.47, 128.80, 127.04, 113.38, 35.95, 21.26.

S-*Phenyl ethanethioate (Table 1, entry 36)*

^{1}H NMR ($CDCl_3$) δ: 7.31 (s, 5H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 193.76, 134.29, 129.26, 129.04, 127.83, 30.01.

Se-*Phenyl ethaneselenoate (Table 1, entry 37)*

^{1}H NMR ($CDCl_3$) δ: 7.44–7.40 (m, 2H), 7.29–7.25 (m, 3H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 196.55, 135.58, 129.24, 128.81, 126.54, 33.90.

S-*Phenyl benzothioate (Table 1, entry 38)*

^{1}H NMR ($CDCl_3$) δ: 8.06 (m, 2H), 7.64–7.46 (m, 8H). ^{13}C NMR ($CDCl_3$) δ: 190.07, 136.54, 135.04, 133.60, 129.47, 129.19, 128.69, 127.42, 127.26.

S-*Phenyl benzoselenoate (Table 1, entry 39)*

^{1}H NMR ($CDCl_3$) δ: 7.96 (m, 2H), 7.65–7.60 (m, 3H), 7.52–7.42 (m, 5H). ^{13}C NMR ($CDCl_3$) δ: 193.33, 138.44, 136.28, 133.84, 129.32, 129.02, 128.89, 127.28, 125.71.

Ethyl 2-(phenylthio)acetate (Table 1, entry 40)

^{1}H NMR ($CDCl_3$) δ: 7.43–7.18 (m, 5H), 4.16 (q, J = 7.2 Hz, 2H), 3.63 (s, 2H), 1.22 (t, J = 7.2 Hz, 3H). ^{13}C

NMR ($CDCl_3$) δ: 169.61, 134.94, 129.94, 128.93, 126.88, 61.45, 36.65, 14.00.

Ethyl 2-(phenylseleno)acetate (Table 1, entry 41)

^1H NMR ($CDCl_3$) δ: 7.59–7.55 (m, 2H), 7.30–7.23 (m, 3H), 4.10 (q, J = 7.2 Hz, 2H), 3.49 (s, 2H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 170.65, 133.23, 129.05, 128.97, 127.63, 61.08, 27.39, 13.86.

2-(Phenylthio)acetophenone (Table 1, entry 42)

^1H NMR ($CDCl_3$) δ: 7.76 (m, 2H), 7.41–7.01 (m, 8H), 4.09 (s, 2H). ^{13}C NMR ($CDCl_3$) δ: 193.72, 135.01, 134.59, 133.18, 129.95, 128.77, 128.38, 128.35, 126.68, 40.80.

1,4-Bis(phenylselanyl)butane[30] (Table 1, entries 19 and 21)

^1H NMR ($CDCl_3$) δ: 7.37–7.34 (m, 4H), 7.16–7.10 (m, 6H), 2.77 (t, 4H), 1.70 (t, 4H). ^{13}C NMR ($CDCl_3$) δ: 132.43, 130.13, 128.87, 126.61, 29.95, 27.01. Calculated for $C_{16}H_{18}Se_2$ (%): C, 52.18; H, 4.93. Found (%): C, 52.23; H, 4.77. MS (70 eV, EI, for ^{80}Se) m/z (%): 369[4] [M –1], 210 (100), 157,[15] 155 (64), 77.[24]

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References

(1) Chadha, R. K.; Hayes, P. C.; Mabrouk, H. E.; Tuck, D. G. *Can. J. Chem.* **1987**, *65*, 804. doi:10.1139/v87-136.
(2) Suh, S.; Hoffman, D. M. *Inorg. Chem.* **1998**, *37*, 5823. doi:10.1021/ic980671m.
(3) Kumar, R.; Mabrouk, H. E.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1988**, 1045. doi:10.1039/dt9880001045.
(4) Briand, G. G.; Davidson, R. J.; Decken, A. *Inorg. Chem.* **2005**, *44*, 9914. doi:10.1021/ic051138r. PMID:16363862.
(5) Green, J. H.; Kumar, R.; Seudeal, N.; Tuck, D. G. *Inorg. Chem.* **1989**, *28*, 123. doi:10.1021/ic00300a028.
(6) Peppe, C.; Tuck, D. G. *Can. J. Chem.* **1984**, *62*, 2798. doi:10.1139/v84-474.
(7) Kuchta, M. C.; Rheingold, A. L.; Parkin, G. *N. J. Chem.* **1999**, *23*, 957. doi:10.1039/a905250j.
(8) Annan, T. A.; Kumar, R.; Mabrouk, H. E.; Tuck, D. G.; Chadha, R. K. *Polyhedron* **1989**, *8*, 865. doi:10.1016/S0277-5387(00)86436-0.
(9) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 3478. doi:10.1021/ic00068a016.
(10) Harris, W. R.; Messori, L. *Coord. Chem. Rev.* **2002**, *228*, 237. doi:10.1016/S0010-8545(02)00037-1.
(11) Ho, T.-L. *Chem. Rev.* **1975**, *75*, 1. doi:10.1021/cr60293a001.
(12) Leverd, P. C.; Ephritikhine, M.; Lance, M.; Vigner, J.; Nierlich, M. *J. Organomet. Chem.* **1996**, *507*, 229. doi:10.1016/0022-328X(95)05773-I.
(13) Barros, O. S. D.; de Carvalho, A. B.; Lang, E. S.; Peppe, C. *Lett. Org. Chem.* **2004**, *1*, 43. doi:10.2174/1570178043488671.
(14) Ranu, B. C.; Mandal, T. *Can. J. Chem.* **2006**, *84*, 762. doi:10.1139/V06-065.
(15) Braga, A. L.; Schneider, P. H.; Paixão, M. W.; Deobald, A. M.; Peppe, C.; Bottega, D. P. *J. Org. Chem.* **2006**, *71*, 4305. doi:10.1021/jo060286b. PMID:16709076.
(16) Peppe, C.; Lang, E. S.; Ledesma, G. N.; de Castro, L. B.; Barros, O. S. D.; Mello, P. D. *Synlett* **2005**, 3091. doi:10.1055/s-2005-921931.
(17) For hydroselenation of alkynols with $IIn(SePh)_2$, see: Barros, O. S. D.; Lang, E. S.; de Oliveira, C. A. F.; Peppe, C.; Zeni, G. *Tetrahedron Lett.* **2002**, *43*, 7921. doi:10.1016/S0040-4039(02)01904-4.
(18) Barros, O. S. D.; Lang, E. S.; Peppe, C.; Zeni, G. *Synlett* **2003,** 1725. doi:10.1055/s-2003-41006.
(19) Ranu, B. C.; Chattopadhyay, K.; Banerjee, S. *J. Org. Chem.* **2006**, *71*, 423. doi:10.1021/jo052087i. PMID:16388676.
(20) Ranu, B. C.; Mandal, T. *J. Org. Chem.* **2004**, *69*, 5793. doi:10.1021/jo0493727. PMID:15307762.
(21) Ranu, B. C.; Mandal, T.; Samanta, S. *Org. Lett.* **2003**, *5*, 1439. doi:10.1021/ol034178c. PMID:12713293.
(22) Peppe, C.; de Castro, L. B.; Mello, M. D.; Barros, O. S. D. *Synlett* **2008**, 1165. doi:10.1055/s-2008-1072725.
(23) Munbunjong, W.; Lee, E. H.; Chavasiri, W.; Jang, D. O. *Tetrahedron Lett.* **2005**, *46*, 8769. doi:10.1016/j.tetlet.2005.10.025.
(24) Bates, C. G.; Gujadhur, R. K.; Venkataraman, D. *Org. Lett.* **2002**, *4*, 2803. doi:10.1021/ol0264105. PMID:12153239.
(25) Krief, A.; Dumont, W.; Gillin, F. *Arkivoc* **2007**, 51.
(26) Yoon, N. M.; Choi, J.; Ahn, J. H. *J. Org. Chem.* **1994**, *59*, 3490. doi:10.1021/jo00091a047.
(27) Cohen, R. J.; Fox, D. L.; Salvatore, R. N. *J. Org. Chem.* **2004**, *69*, 4265. doi:10.1021/jo0401265. PMID:15176857.
(28) Awaleh, M. O.; Badia, A.; Brisse, F.; Bu, X. H. *Inorg. Chem.* **2006**, *45*, 1560. doi:10.1021/ic051357c. PMID:16471967.
(29) Abou, A.; Foubelo, F.; Yus, M. *Arkivoc* **2007**, 196.
(30) Duddeck, H.; Wagner, P.; Rys, B. *Magn. Reson. Chem.* **1993**, *31*, 736. doi:10.1002/mrc.1260310809.
(31) Gulliver, D. J.; Hope, E. G.; Levason, W.; Murray, S. G.; Potter, D. M.; Marshall, G. L. *J. Chem. Soc., Perkin Trans.* **1984**, *2*, 429.
(32) Ranu, B. C.; Samanta, S.; Hajra, A. *Synlett* **2002**, 0987. doi:10.1055/s-2002-31911.
(33) Nishino, T.; Okada, M.; Kuroki, T.; Watanabe, T.; Nishiyama, Y.; Sonoda, N. *J. Org. Chem.* **2002**, *67*, 8696. doi:10.1021/jo026032h. PMID:12444664.
(34) Grieco, P. A.; Yokoyama, Y.; Williams, E. *J. Org. Chem.* **1978**, *43*, 1283. doi:10.1021/jo00400a070.
(35) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. doi:10.1016/0040-4020(78)80135-5.