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Addition of Hydrogen Halides to Acetylenic Selenides. Synthesis of 1-Halo-1-Selenoalkenes

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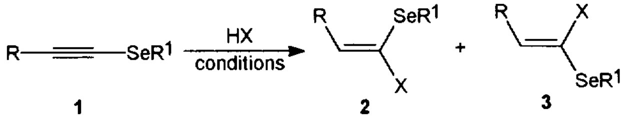
Abstract: Acetylenic selenides react with HX (X=Cl, Br, I) at room temperature to give 1-halo-1-selenoalkenes in good yields. The 1-iodo-1-selenoalkenes were transformed into the corresponding vinylic organometallics (M=Zn, Cu, Cr). Copyright © 1996 Elsevier Science Ltd

Introduction

The addition of inorganic acids to acetylenes has been widely studied and utilized in organic chemistry.[1] The subject continues to attract the attention of the organic chemists, and recent reports in the literature deal with new aspects of this important reaction.[2] Of special interest for us was the report some time ago of the addition of acids to tosylacetylenes.[3] The reaction led to regio- and stereospecific *syn* monoaddition adducts in good yields. The addition of acids to acetylenes linking other atoms of the VIth family to the acetylenic triple bond has received less attention.[4] Recently a detailed study about the addition of *p*-toluensulfonic acid (PTSA) to acetylenic selenides was reported.[5] It was found that this reaction leads to (*Z*)-α-(phenylseleno)vinyl *p*-toluensulfonates, which by reaction with MgX_2 (X=Br, I) are transformed into the corresponding 1-halo-1-selenoalkenes with retention of the double bond geometry.[6] The high regioselectivity of this addition reaction to acetylenic selenides can be attributed to the ability of selenium to stabilize carbenium ions.[7] Concerning the steric course of the reaction, it is known that the experimental conditions greatly affect the final isomer composition.[1] In view of our continued interest in the chemistry of selenoacetylenes,[8] we undertook a systematic investigation of the reaction between hydrogen halides (HCl, HBr, HI) with such compounds.[9] Appropriate manipulation of the resulting 1-halo-1-selenoalkenes could transform them into vinylic selenides, which are versatile building blocks in organic synthesis.[10]

Six acetylenic selenides **(1a-f)** were reacted with HX (X=Cl, Br, I) in anhydrous and aqueous medium under catalytic and noncatalytic conditions (Scheme 1).



1a: $R = C_4H_9$; $R^1 = CH_3$
1b: $R = C_4H_9$; $R^1 = C_6H_5$
1c: $R = C_5H_{11}$; $R^1 = CH_3$
1d: $R = C_5H_{11}$; $R^1 = C_6H_5$
1e: $R = C_6H_5$; $R^1 = CH_3$
1f: $R = C_6H_5$; $R^1 = C_6H_5$

2a, 3a: $R = C_4H_9$; $R^1 = CH_3$; $X = Cl$
2b, 3b: $R = C_4H_9$; $R^1 = CH_3$; $X = Br$
2c, 3c: $R = C_4H_9$; $R^1 = CH_3$; $X = I$
2d, 3d: $R = C_4H_9$; $R^1 = C_6H_5$; $X = Cl$
2e, 3e: $R = C_4H_9$; $R^1 = C_6H_5$; $X = Br$
2f, 3f: $R = C_4H_9$; $R^1 = C_6H_5$; $X = I$
2g, 3g: $R = C_5H_{11}$; $R^1 = CH_3$; $X = Cl$
2h, 3h: $R = C_5H_{11}$; $R^1 = CH_3$; $X = Br$
2i, 3i: $R = C_5H_{11}$; $R^1 = CH_3$; $X = I$

2j, 3j: $R = C_5H_{11}$; $R^1 = C_6H_5$; $X = Cl$
2k, 3k: $R = C_5H_{11}$; $R^1 = C_6H_5$; $X = Br$
2l, 3l: $R = C_5H_{11}$; $R^1 = C_6H_5$; $X = I$
2m, 3m: $R = C_6H_5$; $R^1 = CH_3$; $X = Cl$
2n, 3n: $R = C_6H_5$; $R^1 = CH_3$; $X = Br$
2o, 3o: $R = C_6H_5$; $R^1 = CH_3$; $X = I$
2p, 3p: $R = C_6H_5$; $R^1 = C_6H_5$; $X = Cl$
2q, 3q: $R = C_6H_5$; $R^1 = C_6H_5$; $X = Br$
2r, 3r: $R = C_6H_5$; $R^1 = C_6H_5$; $X = I$

Scheme 1

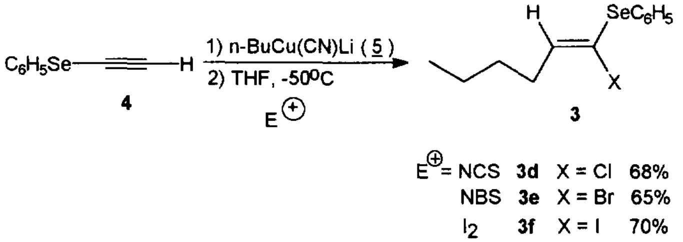
The reaction was first investigated using benzene saturated with gaseous HX (X=Cl, Br) as the reaction medium. Reaction of 1-methylseleno heptyne (**1c**) under these conditions led to the formation of **2h:3h** in a 11.7:1 ratio. Attempts to modify the isomer ratio by heating the reaction mixture under reflux led to decomposition of the products. Reaction of **1c** in benzene/acetic acid (3:1) with aqueous 48% hydrobromic acid at room temperature gave a 10.3:1 ratio of **2h:3h** after 4 h at room temperature. Under $HgCl_2$ catalysis a 13.2:1 ratio of **2h:3h** was observed after 3 h of stirring at room temperature. By maintaining the reaction mixture at room temperature for 24 h or 48 h a 3.2:1 of **2h:3h** was obtained. These experiments showed that the isomer ratio is dependent on the reaction time, and stereochemical control of the addition reaction is difficult, since in some cases it takes a long time to consume all the starting material.

As different isomer ratios were observed in different runs under virtually identical reaction conditions, we presumed that some isomerization could be taking place during the work-up and purification process. In order to address this assumption, for example, we submited samples of pure isomers to experimental conditions that could promote the isomerization. Pure **2q** (obtained by flash chromatography of a mixture of **2q** and **3q** on silica gel eluting with hexane and recrystalization from pentane) was stirred in chloroform in the presence of SiO_2 at room temperature. After 2 h a 2.0:1.0 mixture of **2q** and **3q** was detected. After 12 h under these conditions the **2q:3q** ratio was 1.0:1.0. By refluxing **2q** in chloroform for 1 h a 2.5:1.0 ratio of **2q:3q** was observed, and after 12 h under reflux a 1.0:1.0 ratio of **2q:3q** was produced. By stirring a solution of **2q** in chloroform in the presence of 48% aqueous HBr for 1 h at room temperature a 2.7:1.0 ratio of **2q:3q** was obtained, whereas after 12 h under these conditions the **2q:3q** ratio was 1.0:1.0. Similar results were obtained when pure **3e**, prepared as described in equation 1, was submited to identical conditions.

The above experiments showed that the isomer ratios in Table 1 do not reflect a kinetic preference for a specific isomer, but a balance between kinetic and thermodynamic preferences in each case. Besides the reaction medium, the structure of the substrate and the nature of electrophile can also influence the final isomer mixture composition. In this regard, it should be noted that the stereochemistry of the addition of hydrogen halides to acetylenes is complex because different factors can influence it.[1] Thus, at this stage any rationalization on the stereochemical outcome of the addition of different hydrogen halides to different acetylenic selenides would be speculative and unjustified.

In all cases studied the only regioisomer obtained was that shown in Scheme 1, and no product of hydrolysis of **2** and **3** was detected. From Table 1 the following conclusions can be drawn: The yields of the purified products were in most cases in the range of 75-84%, and isomer **2** predominated in the purified samples. A decrease in the reaction times was observed in the reactions catalyzed by $HgCl_2$. The influence of the nonacetylenic group linked to the selenium atom in the reaction time is noteworthy, with the phenylselenoacetylene requiring a longer reaction time than the methylselenoacetylenes.

The assignment of the stereochemistry of the trisubstituted vinylic selenides by ^{1}H NMR was not trivial. NOE experiments with the mixture of isomers (**2**+**3**) were attempted, but the vinylic signals were not separated sufficiently to give conclusive results. In this way, authentic samples of 1-halo-1-(phenylseleno)-1-hexene (X=Cl, Br, I) were prepared employing a method we recently developed.[8g] This consists of the reaction of phenylselenoacetylene (**4**) with lithium buthylcyanocuprate (**5**), followed by reaction with a halogen source (Eq. 1). Attempts to prepare 1-halo-1-(phenylseleno)-2-phenylethenes by the same method failed.



(1)

Table 1. Addition of HX (X = Cl, Br, I) to Acetylenic Selenides

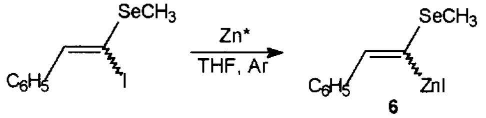
Entry	R	R^1	X	Product	Reaction Conditions	Reaction Time (h)[a]	Yield (%)[b]	Isomer Ratio 2 : 3
1.	C_4H_9	CH_3	Cl	**2a+3a**	A	3.0	75	4.2 : 1[d]
2.					B	1.0	78	4.1 : 1[d]
3.					C	12.0	84	12.8 : 1[d]
4.	C_4H_9	CH_3	Br	**2b+3b**	A	5.0	74	10.8 : 1[d]
5.					B	2.0	76	14.1 : 1[d]
6.					C	12.0	79	12.6 : 1[d]
7.	C_4H_9	CH_3	I	**2c+3c**	A	11.0	80	2.6 : 1[d]
8.					B	9.0	85	2.6 : 1[d]
9.	C_4H_9	C_6H_5	Cl	**2d+3d**	A	11.0	84	15.3 : 1[d]
10.					B	7.0	79	10.8 : 1[d]
11.					C	12.0	82	16.2 : 1[d]
12.	C_4H_9	C_6H_5	Br	**2e+3e**	A	35.0	84	4.8 : 1[d]
13.					B	16.0	80	6.4 : 1[d]
14					C	12.0	83	14.4 : 1[d]
15.	C_4H_9	C_6H_5	I	**2f+3f**	A	32.0	82	5.2 : 1[d]
16.					B	14.0	80	6.3 : 1[d]
17.	C_5H_{11}	CH_3	Cl	**2g+3g**	A	3.0	79	3.6 : 1[d]
18.					B	1.0	78	4.4 : 1[d]
19.					C	12.0	81	11.0 : 1[d]
20.	C_5H_{11}	CH_3	Br	**2h+3h**	A	5.0	76	10.3 : 1[d]
21.					B	2.0	75	13.2 : 1[d]
22.					C	12.0	75	10.1 : 1[d]
23.	C_5H_{11}	CH_3	I	**2i+3i**	A	11.0	80	2. 5 : 1[d]
24.					B	9.0	79	2.7 : 1[d]
25.	C_5H_{11}	C_6H_5	Cl	**2j+3j**	A	11.0	82	16.7 : 1[d]
26.					B	7.0	80	11.2 : 1[d]
27.					C	12.0	75	15.6 : 1[d]
28.	C_5H_{11}	C_6H_5	Br	**2k+3k**	A	35.0	84	5.7 : 1[d]
29.					B	16.0	82	6.2 : 1[d]
30.					C	12.0	83	14.7 : 1[d]
31.	C_5H_{11}	C_6H_5	I	**2l+3l**	A	32.0	84	3.9 : 1[d]
32.					B	16.0	81	6.4 : 1[d]
33.	C_6H_5	CH_3	Cl	**2m+3m**	A	7.0	80	9.1 : 1[c]
34.					B	4.0	80	7.7 : 1[c]
35.					C	12.0	83	1 : 1.7[c]
36.	C_6H_5	CH_3	Br	**2n+3n**	A	12.0	79	5.9 : 1[c]
37.					B	10.0	75	5.9 : 1[c]
38.					C	12.0	72	1 : 2.1[c]
39.	C_6H_5	CH_3	I	**2o+3o**	A	13.0	84	1.4 : 1[c]
40.					B	12.0	80	1.3 : 1[c]
41.	C_6H_5	C_6H_5	Cl	**2p+3p**	A	219.0	78	3.9 : 1[c]
42.					B	49.0	79	6.4 : 1[c]
43.					C	12.0	75	9.8 : 1[c]
44.	C_6H_5	C_6H_5	Br	**2q+3q**	A	234.0	76	8.3 : 1[c]
45.					B	128.0	78	8.5 : 1[c]
46.					C	12.0	82	12.0 : 1[c]
47.	C_6H_5	C_6H_5	I	**2r+3r**	A	128.0	79	13.2 : 1[c]
48.					B	42.0	81	10.5 : 1[c]

Method A: Reaction performed in benzene/HOAc (3 : 1)/aqueous HX (37% HCl, 48% HBr, 51% HI); Method B: Reaction performed in chloroform/aqueous HX (37% HCl, 48% HBr, 51% HI) in the presence of catalytic amounts of $HgCl_2$ (5.0 mol%); Method C: reaction performed in benzene saturated with dry HX (X = Cl, Br). [a]The reaction was monitored by gas chromatography, the time refers to the time necessary to consume all the starting material; [b]Yield of the chromatographed product on a silica gel column eluting with hexane; [c]Isomer ratio determined by gas chromatography; [d]Isomer ratio determined by ^1H NMR spectroscopy.

The 1-halo-1-(phenylseleno)-1-hexenes **(3d-f)** were obtained as single isomers as anticipated by literature precedents.[11] The vinylic protons absorbed as triplets at 6.20 ppm, 6.43 ppm and 6.38 ppm for **3d**, **3e** and **3f** respectively. The coupling constants of the vinylic protons to the neighboring CH_2 protons were 7.1 Hz, 7.0 Hz and 6.9 Hz for **3d**, **3e** and **3f**, respectively. NOE experiments for the bromo and iodo derivatives **3e** and **3f** gave a positive increment for the phenyl protons signals upon irradiation of the vinylic protons, thereby confirming the *cis* arrangement of the vinylic hydrogen and the phenylseleno group. In the case of the chloro derivative **3d**, the NOE effect was negligible. Comparison of the spectra of the pure isomers **3e,f** with the spectra of the isomer mixtures **2e** + **3e and 2f** + **3f** showed that the triplet at higher field (6.49 ppm for X=Br, 6.42 ppm for X=I) in the spectra of the mixtures coincided with the triplet of the pure isomer **3e** and **3f**; the coupling constants to the neighboring CH_2 were of the same magnitude (7.0 Hz and 6.9 Hz, respectively). On the other hand, the triplets at lower field (6.61 ppm for X=Br; 7.03 ppm for X=I) showed a larger coupling constant to the neighboring CH_2 protons (7.5 Hz for X=Br and 7.4 Hz for X=I). These results permitted assignment of the geometry for both isomers of the mixture obtained by addition of HX (X= Br, I) to the phenylselenoacetylene **(4)**. The spectrum of the chloro derivatives **2d** + **3d** showed two triplets with chemical shifts too close (6.27 ppm and 6.28 ppm) to be compared with the chemical shift of the pure isomer **3d** (6.20 ppm). However, one of the signals in the spectrum of the mixture exhibited a coupling constant to the neighboring CH_2 of 7.1 Hz. This is the same coupling constant observed for compound **3d**, which is of the same magnitude of those observed for **3e** and **3f**. The other triplet in the spectrum of the mixture of **2d** + **3d** showed a coupling constant of 7.6 Hz, following the same trend as the bromo and iodo derivatives **3e** and **3f**. (Namely, a larger J is observed for the isomers **2d-f** which have the opposite configuration to that observed for compounds prepared by carbocupration of phenylselenoacetylene i.e., compounds **3d-f**).

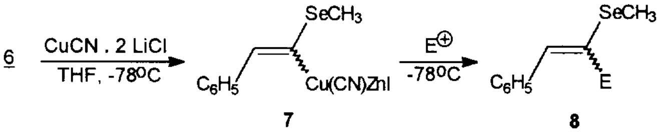
A more general approach to assign the stereochemistry of 1-halo-1-selenoalkenes is derived from the comparison of the ^{77}Se NMR spectra of the mixture of **2** and **3** with that of some authentic samples prepared according to equation 1. Recently we reported a useful method to distinguish between *Z* and *E* vinylic selenides that is based on the relative ^{77}Se chemical shifts of the isomers.[12] The higher field signal in the ^{77}Se NMR spectra of 1-halo-1-selenoalkenes was assigned to the isomer with the alkyl or phenyl group *cis* to the organoseleno group. This difference derives from the γ gauche effect of the substituent, which should be absent in the isomer with the substituent *trans* to the organoseleno moiety. In this work we compared the ^{77}Se NMR spectra of the mixtures with those of the authentic samples prepared by carbocupration of phenylselenoacetylene[8g] and confirmed the prior assignments. In all cases, the selenium atom of the isomer with selenium *cis* to the olefin hydrogen atom absorbed at lower field (347.7-647.9 ppm) than the isomer with selenium *trans* to it (303.8-569.6). On the other hand, the signal assigned to the olefin hydrogen *cis* to the organoselenium moiety appears at higher field than the signal assigned to the isomer with selenium *trans* to it.

1-Halo-1-selenoalkenes are poorly investigated compounds. There are few methods for their preparation,[5,6,8g] and no information about their reactivity is available. However, it has been recently noted that they could be used to effect several conversions.[5] In this work, we investigated the transformation of such compounds into vinylic α-selenoorganometallics and performed the reaction of these species with electrophiles. The first reaction investigated was the insertion of activated zinc powder into the sp^2 carbon-halogen bond. Zinc powder previously activated by reaction with 1,2-dibromoethane and Me_3SiCl was used and the reaction was performed under argon (Eq. 2).[13] The reaction was monitored by sampling the reaction mixture followed by hydrolysis and gas chromatography. Formation of **6** was confirmed by hydrolysis of the reaction mixture with saturated ammonium chloride solution and isolation of the product **8d**. The 1-chloro- and 1-bromo-1-selenoalkenes were inert toward activated zinc even at higher temperatures and longer reaction times.



(2)

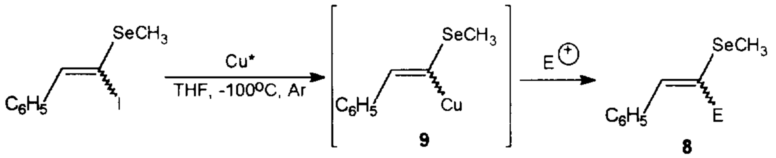
The organozinc compound **6** exhibited low reactivity, and it underwent reaction with electrophiles only after the transmetallation with CuCN•2 LiCl[14] to give intermediate 7. The transmetallation reaction was performed by adding a solution of CuCN•2 LiCl in THF via cannula to the organozinc compound **6** at -78 °C. After a few minutes of stirring the electrophile was added leading to products **8** with the yields showed in Table 2 (Eq. 3).



(3)

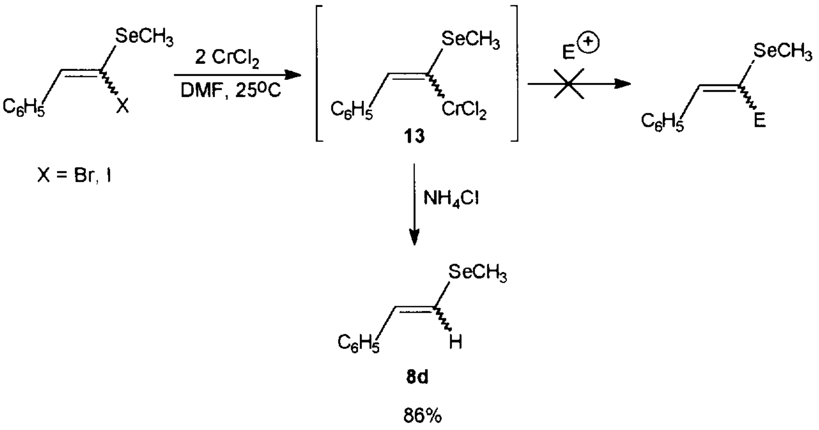
Less reactive electrophiles, such as alkyl halides, aldehydes, ketones and epoxides failed to react even in the presence of Lewis acids ($BF_3•Et_2O$, Me_3SiCl) and co-solvents such as HMPA and DMF. The reaction was non-stereoselective leading to *Z* and *E* olefins, even when the starting 1-iodo-1-selenoalkene was isomerically pure.

Reaction of 1-iodo-1-(methylseleno)-2-phenyl ethene with activated copper,[15] which was prepared by adding lithium naphthalenide to a solution of CuCN•2 LiCl in THF at -100 °C under argon gave the vinylcopper **9** which reacted with electrophiles giving the products **8** in good yields (Eq. 4, Table 2).



(4)

Finally, reaction of 1-bromo-1-(methylseleno)-2-phenylethene and 1-iodo-1-(methylseleno)-2-phenylethene with chromium chloride in DMF at room temperature gave intermediate **13**. The reaction was exothermic with 1-iodo-1-(methylseleno)-2-phenylethene. Formation of intermediate **13** was confirmed by hydrolysis of the reaction mixture and identification of product **8d**. However, reaction of **13** with electrophiles **11** and **12** was unsuccessful (Scheme 2).



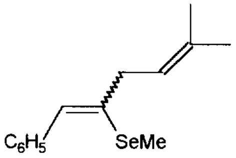
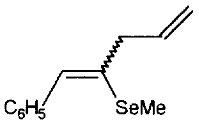
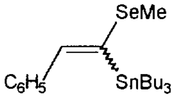
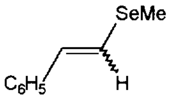
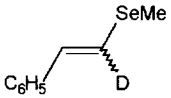
Scheme 2

Conclusion

The addition of hydrogen halides to acetylenic selenides is a good method to prepare 1-halo-1-seleno alkenes, although the reaction proceeded with no stereochemical control. Nevertheless, the feasibility of transforming such compounds into vinylic selenides with chain elongation as demonstrated in this work, allow their use in synthetic transformations in which the carbon-carbon double bond is not maintained.[10] Alternative methods to perform the chain elongation of 1-halo-1-seleno alkenes are underway in our group and will be reported soon. Our carbocupration-halogenation method of phenylselenoacetylene leading to isomerically pure 1-halo-1-selenoalkenes complements the recently published method to prepare such compounds with the opposite stereochemistry.[5]

Table 2

$$7 \xrightarrow{E^{\oplus}} 8 \xleftarrow{E^{\oplus}} 9$$

Organometallic	E^+	Time (h)	**8**	Yield (%)
7	 **10**	12	 **8a**	60
9	**10**	3	**8a**	70
7	 **11**	12	 **8b**	66
9	**11**		**8b**	68
7	Bu_3SnCl **12**	12	 **8c**	71
9	**12**	3	**8c**	80
7	NH_4Cl	a	 **8d**	95
9	NH_4Cl	a	**8d**	90
7	D_2O	a	 **8e**	95
9	D_2O	a	**8e**	90

[a] The electrophile was added at -78 °C, the mixture was allowed to reach room temperature and then worked-up.

Experimental Section

General: ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer with tetramethylsilane as the standard. ^{13}C NMR spectra were obtained on a Bruker AC-200 spectrometer using the central peak of $CDCl_3$ (77.0 ppm) as standard. ^{77}Se NMR spectra were recorded at 38.14 MHz in a Bruker AC-200F spectrometer with multinuclear 10 mm VSP probe in 10 mm tubes containing c.a. 400 mg sample in $CDCl_3$

solution and sealed tube containing as the standard, 0.5 mL of a 1% Me_2Se solution in $CDCl_3$, in a co-axial arrangement. IR spectra were recorded on a Perkin Elmer 1600 spectrophotometer. Low resolution mass spectra were obtained on a Finnigan 4021 spectrometer or on a GC/MS-Hewlett Packard 5988-8/5890 spectrometer, both operating at 70 eV. Elemental analysis were performed at the Microanalytical Laboratory of the Institute of Chemistry - USP. Column chromatography were carried out with Merck silica-gel (230-400 mesh) according to the procedure by Still and coworkers.[16] Thin layer chromatography (TLC) was performed on silica-gel 60 F-254 on aluminum. All solvents used were previously dried and distilled according to the usual methods.[17] THF was distilled from sodium/benzophenone under N_2, immediately before use. Selenium (320 mesh) was purchased from Aldrich, CuCN was obtained from Aldrich and dried under vacuum in an Abderhalden apparatus over P_2O_5. *n*-BuLi (in hexane solution) was purchased from Aldrich and titrated[18] prior to use. The remaining chemicals were obtained from commercial sources. All operations involving organometallics were carried out in flame dried glassware, under an inert atmosphere of dry and deoxygenated argon. The acetylenic selenides **1a-f** were prepared by described methods.[8]

Preparation of Phenylselenoacetylene (4):[8g] A dry three-necked round bottomed flask under argon atmosphere, equipped with a magnetic stirring bar, containing a solution of *n*-butyl magnesium bromide (20.0 mmol) in THF (100 mL) was cooled to -78 °C. Acetylene (free from acetone by passing through two cold traps) was bubbled through this solution until the color turned into violet. Then the acetylene bubbling was stopped, and the reaction mixture was allowed to warm to room temperature under vigorous stirring, followed by dropwise addition of phenylselenyl bromide (4.72 g, 20.0 mmol) in THF (50 mL). After 30 min, the reaction mixture was quenched with saturated solution of NH_4Cl. The product was extracted with hexane, washed with brine and dried over anhydrous $MgSO_4$. The product was purified by flash silica gel chromatography eluting with hexane. Yield: 3.9 g (78%). bp °C 60 °C / 0.20 mm Hg. ^1H NMR (200 MHz, $CDCl_3$) δ 3.14 (s, 1H), 7.2-7.6 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 64.5, 91.5, 127.15, 129.0, 129.1, 129.2, 129.3, 129.4. IR (film): 3283, 3069, 2035, 1579, 1477, 1440, 1068, 1021, 735, 687, 669, 578. LRMS (rel. int.) m/z 182 (50), 180 (25), 102 (100), 77 (46), 51 (41), 50 (19). Anal. Calcd. for C_8H_6Se: C, 53.06, H, 3.34. Found: C, 53.11, H, 3.66.

Addition of Hydrogen Halides to Selenoacetylenes. In Aqueous Medium: In a flask containing the selenoacetylene **1** (10.0 mmol) in benzene/acetic acid (3:1; 15 mL) at room temperature was added concentrated hydrogen halide (37% HCl, 48% HBr, 51% HI, 3 mL). The reaction mixture was stirred at room temperature for the time indicated in Table 1 and the progress of the reaction was monitored by gas chromatography. After all the selenoacetylene **1** was consumed, the mixture was diluted with hexane (50 mL), the organic phase was washed with saturated $NaHCO_3$ and dried with $MgSO_4$. The solvent was evaporated under vacuum and the residue was purified by flash chromatography on silica gel eluting with hexane. For reaction times see Table 1. The same procedure was used in the reaction catalyzed by $HgCl_2$ (0.135 g; 0.5 mmol) using chloroform (50 mL) as the solvent. For reaction times see Table 1.

In Anhydrous Medium: Anhydrous HX (X=Cl, Br) was bubbled through a solution of the selenoacetylene **1** (10.0 mmol) in benzene (25 mL) at room temperature for 1 h. Then the mixture was stirred for the time indicated in Table 1, and the reaction was monitored by gas chromatography. After all the starting selenoacetylene **1** was consumed, the mixture was washed with saturated solution of $NaHCO_3$ and worked-up as describe above. For reaction times see Table 1.

1-Chloro-1-(methylseleno)-1-hexene (2a + 3a): (1.77g, 84%) ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, *J*=6.5 Hz, 3H), 1.3 (m, 4H), 2.2 (m, 2H), 2.24 (s, 3H), 2.25 (s, 3H), 6.30 (t, *J*=6.9 Hz, 1H), 6.37 (t, *J*=7.6 Hz, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.7, 9.9, 13.9, 22.1, 22.2, 30.3, 30.8, 32.8, 32.9, 33.0, 107.1, 108.4, 138.8, 141.5. IR (film): 3055, 3023, 2931, 1599, 1569, 1491, 1445, 1424, 1273, 921, 879, 790, 749, 749, 693, 520. LRMS (rel. int.) m/z 212 (35), 197 (7), 156 (19), 133 (16), 116 (13), 107 (10), 93 (21), 81 (100), 75 (18), 53 (19). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 267.2, 347.7. Anal. Calcd. for $C_{12}H_{15}SeCl$: C, 39.74, H, 6.19. Found: C, 39.97, H, 6.33.

1-Bromo-1-(methylseleno)-1-hexene (2b + 3b): (2.02g, 79%) ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, *J*=6.7 Hz, 3H), 1.35 (m, 4H), 2.2 (m, 2H), 2.27 (s, 3H), 6.05 (t, *J*=7.1 Hz, 1H), 6.06 (t, *J*=7.6 Hz, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 7.7, 8.1, 13.8, 22.1, 22.2, 29.8, 30.4, 31.0, 31.5, 118.3, 119.1, 135.8, 136.1. IR (film) 2957, 2927, 2871, 2858, 1578, 1477, 1465, 1439, 1022, 1000, 804, 766, 736, 689. LRMS (rel. int.) m/z 256 (21), 213 (14), 177 (6), 133 (12), 119 (7), 81 (100), 67 (2), 53 (7). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 295.60, 379.90. Anal. Calcd. for $C_7H_{13}SeBr$: C, 33.03, H, 5.14. Found: C, 33.03, H, 5.14.

1-Iodo-1-(methylseleno)-1-hexene (2c + 3c): (2.65g, 85%) ^1H NMR (200 MHz, $CDCl_3$) δ 0.84 (t, *J*=6.7 Hz, 3H), 1.3 (m, 4H), 2.1(m, 2H), 2.16 (s, 3H), 2.17 (s, 3H), 6.13 (t, *J*=6.8 Hz, 1H), 6.72 (t, *J*=7.4 Hz, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.9, 13.4, 22.1, 29.7, 30.0, 30.5, 32.7, 34.6, 37.8, 77.6, 80.9, 143.8, 150.2. LRMS (rel. int) m/z 304 (12), 261 (2), 177 (2), 135 (20), 119 (10), 81 (100), 53 (22). IR (film) 3030, 2926, 1480, 1427, 1027, 1010, 692, 476. ^{77}Se NMR (38 MHz, $CDCl_3$) δ 335.40, 426.80. Anal. Calcd. for $C_7H_{13}SeI$: C, 27.27, H, 4.29. Found: C, 28.21, H, 4.43.

1-Chloro-1-(phenylseleno)-1-hexene (2d + 3d): (2.29g, 84%) ^1H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, *J*=2.8 Hz, 3H), 1.2-1.5 (m, 4H), 2.2-2.4 (m, 2H), 6.27 (t, *J*=7.6 Hz, 1H), 6.28 (t, *J*= 7.1 Hz, 1H), 7.2-7.5 (m, 5H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 22.2, 22.3, 30.2, 30.3, 31.0, 32.2, 119.4, 127.6, 127.7, 129.2, 132.5, 140.7. IR (film) 3073, 3059, 2928, 2871, 2858, 1579, 1477, 1439, 831, 735, 689. LRMS (rel. int.) m/z 274 (72), 230 (8), 239 (5), 195 (43), 115 (100), 77 (48). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 467.40, 554.91. Anal. Calcd. for $C_{12}H_{13}SeCl$: C, 52.67, H, 5.53. Found: C, 53.01, H, 5.38.

1-Bromo-1-(phenylseleno)-1-hexene (2e + 3e): (2.67g, 84%) ^1H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, *J*=2.8 Hz, 3H), 1.3-1.5 (m, 4H), 2.2-2.3 (m, 2H), 6.49 (t, *J*=6.9 Hz, 1H), 6.61 (t, *J*= 7.5 Hz, 1H), 7.2-7.5 (m, 5H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 22.1, 29.7, 30.1, 33.0, 33.4, 127,6, 127.7, 129.2, 132.2, 132.3, 143.7, 145.6. IR (film) 2957, 2927, 2871, 2858, 1578, 1477, 1465, 1439, 1022, 1000, 804, 766, 736, 689. LRMS (rel. int.) m/z 318 (14), 275 (4), 236 (2), 195 (13), 115 (57), 81 (100). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 493.90, 584.10. Anal. Calcd. for $C_{12}H_{13}SeBr$: C, 45.32, H, 4.72. Found: C, 45.57, H, 4.83.

1-Iodo-1-(phenylseleno)-1-hexene (2f + 3f): (2.99g, 82%) ^1H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, *J*=1.4 Hz, 3H), 1.3-1.5 (m, 4H), 2.1-2.3 (m, 2H), 6.4 (t, *J*=6.9 Hz, 1H), 7.03 (t, *J*= 7.4 Hz, 1H), 7.3-7.6 (m, 5H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 22.2, 30.6, 35.0, 35.1, 38.2, 74.5, 79.4, 127.6, 129.8, 129.2, 129.3, 132.4, 132.6, 148.5, 153.3. IR (film) 3030, 2936, 1480, 1427, 1027, 1010, 692, 476. LRMS (rel. int.)

m/z 366 (26), 239 (5), 157 (28), 81 (100), 77 (37). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 538.5, 633.0 Anal. Calcd. for $C_{12}H_{13}SeI$: C, 39.48, H, 4.14. Found: C, 39.84, H, 3.86.

1-Chloro-1-(methylseleno)-1-heptene (2g + 3g): (1.78g, 79%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, *J*=6.7 Hz, 3H), 1.3-1.4 (m, 6H), 2.2 (m, 2H), 2.26 (s, 3H), 6.05 (t, *J*=7.6 Hz, 1H), 6.06 (t, *J*= 6.7 Hz, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 7.7, 13.8, 22.3, 28.4, 31.1, 31.7, 118.3, 119.2, 135.7, 136.7. IR (film) 2958, 2928, 2857, 1427, 814, 422. LRMS (rel. int.) m/z 226 (43), 211 (13), 190 (2), 169 (79), 133 (30), 95 (100). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 267.28, 347.51. Anal. Calcd. for $C_8H_{15}SeCl$: C, 45.29, H, 6.70. Found: C, 42.12, H, 6.66.

1-Bromo-1-(methylseleno)-1-heptene (2h + 3h): (2.05g, 76%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9 (t, *J*=6.8 Hz, 3H), 1.3-1.5 (m, 6H), 2.1-2.2 (m, 2H), 2.3 (m, 2H), 6.18 (t, *J*=6.9 Hz, 1H), 6.30 (t,, *J*= 7.5 Hz, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.9, 14.0, 27.8, 28.4, 31.2, 33.0, 33.2, 106.9, 139.0, 142.0. IR (film) 2957, 2857, 1461, 1426, 814, 784, 762. LRMS (rel. int.) m/z 270 (11), 255 (2), 191 (2), 173 (2), 95 (100). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 296.21, 379.80. Anal. Calcd. for $C_8H_{15}SeBr$: C, 35.57, H, 5.60. Found: C, 34.98, H, 5.34.

1-Iodo-1-(methylseleno)-1-heptene (2i + 3i): (2.53g, 80%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9 (t, *J*=6.8 Hz, 3H), 1.3-1.5 (m, 6H), 2.0-2.2 (m, 2H), 2.2 (s, 3H), 6.2 (t, *J*=6.8 Hz, 1H), 6.8 (t, *J*= 7.4 Hz, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.9, 14.0, 22.4, 28.1, 31.2, 34.9, 38.1, 77.5, 80.9, 143.9, 150.3. IR (film) 2956, 2925, 2845, 1421, 905, 775, 745, 725. LRMS (rel. int.) m/z 318 (12), 191 (3), 95 (100). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 426.27, 335.21. Anal. Calcd. for $C_8H_{15}SeI$: C, 30.30, H, 4.77. Found: C, 29.87, H, 4.56.

1-Chloro-1-(phenylseleno)-1-heptene (2j + 3j): (2.35g, 82%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.6 Hz, 3H), 1.3-1.4 (m, 6H), 2.2-2.3 (m, 2H), 6.26 (t, *J*=7.6 Hz, 1H), 6.28 (t, *J*= 7.2 Hz, 1H), 7.2-7.3 (m, 3H), 7.4-7.5 (m, 2H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 22.3, 28.5, 31.1, 32.3, 118.5, 119.4, 127.5, 127.6, 129.1, 132.4, 140.7, 140.8. IR (film) 2963, 2935, 2874, 1602, 1492, 1456, 751, 692. LRMS (rel. int.) m/z 288 (35), 157 (24), 132 (3), 95 (100), 77 (37). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 555.02, 467.38. Anal. Calcd. for $C_{13}H_{17}SeCl$: C, 54.20, H, 5.96. Found: C, 54.45, H, 6.02.

1-Bromo-1-(phenylseleno)-1-heptene (2k + 3k): (2.78g, 84%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, *J*=6.5 Hz, 3H), 1.2-1.4 (m, 6H), 6.50 (t, *J*=6.6 Hz, 1H), 6.68 (t, *J*= 7.5 Hz, 1H), 7.2-7.3 (m, 3H), 7.4-7.5 (m, 2H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 22.3, 28.3, 30.9, 33.6, 105.8, 107.2, 127.8, 127.9, 128.1, 128.5, 143.6, 145.6. IR (film) 2957, 2927, 2856, 1475, 1438, 734, 689. LRMS (rel. int.) m/z 332 (20), 253 (2), 176 (4), 157 (28), 95 (100), 77 (44). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 584.69, 494.18. Anal. Calcd. for $C_{13}H_{17}SeBr$: C, 46.69, H, 3.89. Found: C, 46.86, H, 3.92.

1-Iodo-1-(phenylseleno)-1-heptene (2l + 3l): (3.18 g, 84%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, *J*= 1.8 Hz, 3H), 1.26-1.56 (m, 6H), 2.1 (m, 2H), 2.3 (m, 2H), 6.39 (t, *J*=5.3 Hz, 1H), 7.01 (t, *J*= 7.5 Hz, 1H), 7.3-7.4 (m, 3H), 7.4-7.5 (m, 2H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.3, 28.1, 30.4, 35.3, 38.3, 126.5, 127.6, 127.7, 128.4, 128.8, 129.2, 123.9, 132.4, 132.6, 135.3, 148.5, 153.3. IR (film) 2995, 1474, 1438, 735, 688. LRMS (rel. int.) m/z 380(9), 253 (3), 176 (2), 157 (13), 95 (100), 77 (16). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 633.32, 538.63. Anal. Calcd. for $C_{13}H_{17}SeI$: C, 41.18, H, 4.52. Found: C, 41.08, H, 4.46.

1-Chloro-1-(methylseleno)-2-phenylethene (2m +3m): (1.85g, 80%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.37 (s, 3H), 7.1-7.6 (m, 5H), 6.97 (s, 1H), 7.16 (s, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 8.7, 9.3, 121.9, 127.5, 127.7, 128.0, 128.2, 128.4, 128.5, 131.0, 133.7, 134.7, 135.3. IR(film) 3100, 3081, 3056, 3023, 2932, 1585, 1566, 1492, 1444, 1424, 1269, 879, 845, 800, 748, 694. LRMS (rel. int.) m/z 232 (82), 217 (32), 197 (6), 182 (83), 136 (12), 102 (100). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 303.80, 377.83. Anal. Calcd. for C_9H_9SeCl: C, 46.69, H, 3.89. Found: C, 47.04, H, 4.05.

1-Bromo-1-(methylseleno)-2-phenylethene (2n + 3n): (2.18g, 79%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.30 (s, 3H), 7.3-7.4 (m, 5H), 7.28 (s, 1H), 7.48 (s, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.4, 11.9, 122.5, 127.7, 127.8, 128.0, 128.3, 128.5, 129.0, 133.9, 136.4, 138.5. IR (film) 3023, 2929, 1582, 1563, 1493, 1443, 1422, 1269, 920, 865, 767, 743, 692, 580. LRMS (rel. int.) m/z 276 (61), 197 (16), 182 (16), 102 (100). ^{77}Se

NMR (38 MHz, $CDCl_3$) δ 330.52, 405.18. Anal. Calcd. for C_9H_9SeBr: C, 39.17, H, 3.26. Found: C, 39.48, H, 3.23.

1-Iodo-1-(methylseleno)-2-phenylethene (2o + 3o): (2.71g, 84%) ^1H NMR (200 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.35 (s, 3H), 7.3-7.5 (m, 5H), 7.27 (s, 1H), 7.90 (s, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.7, 16.1, 80.7, 82.1, 127.9, 128.1, 128.2, 128.5, 138.2, 138.5, 146.5. IR (film) 3078, 3054, 3021, 2923, 1598, 1578, 1490, 1442, 1417, 1074, 853, 770, 755, 736, 693, 571. LRMS (rel. int.) m/z 324 (14), 197 (47), 182 (34), 102 (100), ^{77}Se NMR (38 MHz, $CDCl_3$) δ 364.98, 443.29. Anal. Calcd. for C_9H_9SeI: C, 33.47, H, 2.78. Found: C, 33.69, H, 2.66.

1-Chloro-1-(phenylseleno)-2-phenylethene (2p + 3p): (2.29g, 78%) ^1H NMR (200 MHz, $CDCl_3$) δ 7.3-7.6 (m, 10H), 7.32 (s, 1H), 7.55 (s, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 122.1, 127.1, 128.1, 128.3, 128.5, 128.8, 129.0, 129.1, 129.5, 131.7, 133.7, 133.9, 135.5, 136.6. IR (film) 2954, 2925, 2855, 1376, 691. LRMS (rel. int.) m/z 294 (50), 259 (23), 178 (100), 102 (73), 77 (33). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 501.42, 583.53. Anal. Calcd. for $C_{14}H_{11}SeCl$: C, 57.26, H, 3.78. Found: C, 57.63, H, 3.84.

1-Bromo-1-(phenylseleno)-2-phenylethene (2q + 3q): (1.79g, 53%), ^1H NMR (200 MHz, $CDCl_3$) δ 7.3 -7.5 (m, 10H), 7.36 (s, 1H), 7.63 (s, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 109.4, 108.0, 128.2, 128.4, 128.6, 129.1, 129.4, 130.2, 133.5, 133.7, 136.4, 137.3, 141.2. IR (film) 3057, 3024, 1577, 1477, 1071, 1023, 863, 768, 738, 691. LRMS (rel. int.) m/z 338 (30), 340 (23), 259 (32), 182 (13), 178 (100), 102 (64), 77 (35). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 527.97, 608.11. Anal. Calcd. for $C_{14}H_{11}SeBr$: C, 49.73, H, 3.28. Found: C, 50.07, H, 3.45.

1-Iodo-1-(phenylseleno)-2-phenylethene (2r + 3r): (3.04g, 79%) ^1H NMR (200 MHz, $CDCl_3$) δ 7.3-7.6 (m, 10H), 7.34 (s, 1H), 8.04 (s, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 79.9, 80.2, 128.2, 128.3, 128.4, 128.5, 129.2, 129.5, 132.9, 133.9, 134.2, 138.1, 141.7, 148.5. IR (film) 3055, 3021, 1576, 1491, 1476, 1440, 1070, 1022, 855, 757, 735, 690, 669. LRMS (rel. int.) m/z 386 (42), 259 (100), 179 (43), 102 (36), 77 (36). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 569.59, 647.89. Anal. Calcd. for $C_{14}H_{11}SeI$: C, 43.67, H, 2.86. Found: C, 44.11, H, 2.89.

Carbocupration/Halogenation of Phenylselenoacetylene (4): To a dry two-necked flask equipped with a magnetic stirring bar containing copper cyanide (0.24 g; 2.79 mmol) under argon atmosphere was added THF (10 mL). The suspension was cooled to -78 °C and then *n*-BuLi (1.12 mL; 2.75 mmol of a 2.45 M solution in hexane) was added. After 15 min of stirring the mixture was allowed to warm to -50 °C, and a solution of phenylselenoacetylene **(4)** (0.362 g; 2.0 mmol) in THF (2 mL) was added. After 1 h at this temperature the reaction mixture was warmed to -25 °C, the electrophile (NBS, NCS or I_2, 2.5 mmol) was added and then it was stirred for 2 h. After this time, the mixture was treated with saturated NH_4Cl solution, extracted with hexane, washed with NH_4OH solution and brine and the organic phase was dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by silica gel flash chromatography eluting with hexane.

(*E*)-1-Chloro-1-(phenylseleno)-1-hexene (3d): (0.51g, 70%) ^1H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, *J*=6.6 Hz, 3H), 1.1-1.4 (m, 4H), 2.12 (m, 2H), 6.20 (t, *J*=7.1 Hz, 1H), 7.0-7.5 (m, 5H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 22.2, 30.2, 30.3, 118.9, 127.7, 129.6, 132.4, 140.6. IR (film) 2958, 2927, 2861, 1578, 1474, 1429, 735, 689. LRMS (rel. int.) m/z 274 (72), 230 (8), 239 (5), 195 (43), 115 (100), 77 (48). ^{77}Se NMR (38 MHz, $CDCl_3$) δ 554.88. Anal. Calcd. for $C_{12}H_{15}SeCl$: C, 39.48, H, 4.14. Found: C, 52.59, H, 5.32.

(*Z*)-1-Bromo-1-(phenylseleno)-1-hexene (3e): (0.41g, 65%) ^{1}H NMR (200 MHz,CDCl$_3$) δ 0.85 (t, *J*=6.0 Hz, 3H), 1.1-1.4 (m, 4H), 2.18 (m, 2H), 6.41 (t, *J*=7.0 Hz, 1H), 7.1-7.6 (m, 5H), ^{13}C NMR (50 MHz, CDCl$_3$) δ 13.8, 22.2, 30.1, 33.0, 107.1, 127.7, 129.2, 132.4, 143.7. IR (film) 2958, 2927, 2862, 1473, 1439, 735, 689. LRMS (rel. int.) m/z 318 (14), 275 (4), 236 (2), 195 (13), 115 (57), 81 (100). ^{77}Se NMR (38 MHz, CDCl$_3$) δ 584.00. Anal. Calcd. for $C_{12}H_{15}SeBr$: C, 45.31, H, 4.75. Found: C, 45.18, H,4.80.

(*Z*)-1-Iodo-1-(phenylseleno)-1-hexene (3f): (0.37g, 68%) ^{1}H NMR (200 MHz,CDCl$_3$) δ 0.91 (t, *J*=6.0 Hz, 3H), 1.0-1.5 (m, 4H), 2.16 (m, 2H), 6.38 (t, *J*=6.9 Hz, 1H), 7.2-7.3 (m, 3H), 7.4-7.5 (m, 2H), ^{13}C NMR (50 MHz, CDCl$_3$) δ 13.9, 22.2, 30.0, 38.1, 79.4, 127.0, 129.2, 132.5, 132.7, 148.5. IR (film) 2957, 2926, 2861, 1578, 1472, 1022, 735, 689, 470. LRMS (rel. int.) m/z 366 (26), 239 (5), 157 (28), 81 (100), 77 (37). ^{77}Se NMR (38 MHz, CDCl$_3$) δ 691.98. Anal. Calcd. for $C_{12}H_{15}SeI$: C, 52.67, H, 5.52. Found: C, 39.88, H, 3.90

Isomerization Experiments. In silica gel: Pure (*E*)-1-bromo-1-(phenylseleno)-2-phenylethene **(2q)** (0.34 g, 1.0 mmol) and silica gel (1.0 g) in chloroform (10 mL) were stirred at room temperature. The isomerization reaction was monitored by sampling the mixture from time to time and analyzing the samples by gas chromatography. After 2 h of stirring the **2q:3q** ratio was 2.0:1.0; after 12 h the **2q:3q** ratio was 1.0:1.0. The same procedure was applied to pure (*Z*)-1-bromo-1-(phenylseleno)-1-hexene **(3e)**. After 3 h of stirring the **2e:3e** ratio was 5.2:1 and after 12 h the **2e:3e** ratio was 1:1.

Under Acidic Condition: Pure **2q** (0.34 g, 1.0 mmol) in chloroform (10 mL) was stirred at room temperature in the presence of aqueous 48% HBr (1 mL). The reaction was monitored as described above. After 1 h of stirring the **2q:3q** ratio was 2.7:1.0 and after 12 h the **2q:3q** ratio was 1.0:1.0. The same procedure was applied to pure (*Z*)-1-bromo-1-(phenylseleno)-1-hexene **3e**. After 2 h of stirring the **2e:3e** ratio was 3.1:1 and after 12 h the **2e:3e** ratio was 1:1.

Under heating: Pure **2q** (0.34 g, 1.0 mmol) in chloroform (10 mL) was stirred under reflux. The progress of the isomerization was monitored as above. After 1 h under reflux the **2q:3q** ratio was 2.5:1.0 and after 12 h the **2q:3q** ratio was 1.0:1.0. Similar results were obtained when pure **3e** was submited to similar conditions.

Metallation of 1-Halo-1-Selenoalkenes. Reaction with Activated Zinc: A dry, three-necked flask under argon and magnetic stirring bar was charged with zinc power (0.19 g, 3.0 mmol) and flushed with argon. A solution of 1,2-dibromoethane (0.02 g; 0.1 mmol) in THF (2 mL) was then added. The resulting zinc suspension was heated to boiling and then cooled to room temperature. This process was repeated three times. Chlorotrimethylsilane (0.02 g, 0.1 mmol) was then added and after stirring for 10 min at room temperature, a solution of 1-iodo-1-(methylseleno)-2-phenylethene (0.323 g; 1.0 mmol) in THF (2 mL) was added dropwise over a 10 min period. The temperature of the reaction mixture reached 40 °C during the addition. The reaction mixture was stirred for 2 h at room temperature and the progress of the reaction was monitored by gas chromatography. The yields were estimated by quenching the reaction mixture with saturated solution of ammonium chloride and isolating **8d**.

Transmetallation of the Zinc Reagent (6) with CuCN: To a dry flask under argon atmosphere and magnetic stirring bar charged with lithium chloride (0.085 g, 2.0 mmol, previously dried under vacuum at 120 °C for 2 h) and copper cyanide (0.087 g, 1.0 mmol) was added THF (2 mL). The resulting yellowish solution was cooled to -78 °C and the zinc reagent **(6)**, prepared as described above, was slowly added *via* cannula. The reaction mixture was allowed to warm to -20 °C for a 5 min and then cooled again to -78 °C. The appropriate electrophile (3.0 mmol) was added, and after 1 h of stirring at -78 °C the mixture was allowed to warm to -20 °C and maintained at this temperature for the time indicated in Table 2. Then the mixture was treated with saturated solution of NH_4Cl (50 mL) and NH_4OH (50 mL), extracted with hexane (30 mL) and the organic layer was washed with brine and dried with $MgSO_4$. The solvents were evaporated and the residue was purified by flash silica gel chromatography eluting with hexane. For yields and reaction time see Table 2.

Reaction with Activated Copper: To a dry flask under argon and magnetic stirring charged with copper cyanide (0.21 g; 2.4 mmol) and lithium chloride (0.20 g; 4.8 mmol, previously dried under vacuum at 120 °C for 2 h) was added THF (3 mL).

In another flask were placed lithium (0.02 g; 2.6 mmol), naphthalene (0.35 g; 2.6 mmol) and THF (2 mL); the metallic lithium was consumed in few minutes under sonication, giving rise to a green solution of LiNp.

The yellowish solution of CuCN•2 LiCl, prepared as described above was cooled to -78 °C and then transferred *via* cannula to the green LiNp solution which was held at -100 °C, and the mixture was stirred at this temperature for 10 min. 1-Iodo-1-(methylseleno)-2-phenylethene (0.323 g; 1.0 mmol) was weighed into a 5 mL vial; THF (1 mL) was added to the vial under argon. The solution was cooled to -78 °C and then added *via* cannula to the activated copper solution prepared above which was held at -100 °C. The electrophile (2.0 mmol) was added to the mixture at -78 °C, the reaction mixture was heated to 0 °C, stirred at this temperature and then treated with saturated NH_4Cl solution (50 mL), extracted with hexane and the organic layer was washed with saturated NH_4OH solution (50 mL) brine and dried with $MgSO_4$. The solvents were evaporated and the residue was purified by flash silica gel chromatography eluting with hexane. For yields and reaction times see Table 2.

1-phenyl-2-(methylseleno)-5-methyl-1,4-hexadiene (8a): (0.159, 60%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.47 (s, 3H), 1.67 (s, 3H), 2.13 (s, 3H), 3.19 (d, *J*= 6.7 Hz, 2H), 5.16 (t, *J*= 6.7 Hz, 1H), 6.46 (s, 1H), 7.2 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) 4.6, 5.6, 17.8, 17.9, 25.6, 26.8, 32.6, 37.4, 112.2, 121.4, 121.8, 125.9, 126.5, 126.6, 127.4, 127.8, 127.9, 128.1, 137.1, 137.5, 137.7. IR (film) 3079, 3054, 3021, 2924, 1597, 1490, 1442, 1418, 1270, 918, 855, 755, 734, 693, 574, 500. LRMS (rel. int.) m/z 266 (6), 251 (8), 155 (7), 115 (8), 91 (100). Anal. Calcd. for $C_{14}H_{18}Se$: C, 63.39, H, 6.84. Found: C, 63.28, H, 6.97.

1-phenyl-2-(methylseleno)-1,4-pentadiene (8b): (0.156g, 66%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.24 (s, 3H), 3.30 (d, *J*= 6.0 Hz, 2H), 5.2 (m, 1H), 6.59 (s, 1H), 7.0-7.4 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) 4.9, 6.0, 37.8, 42.7, 116.7, 116.8, 126.5, 127.2, 127.5, 128.2, 128.3, 129.4, 132.4, 134.9, 135.2, 136.0, 137.6. IR (film) 3077, 3056, 3020, 2978, 1638, 1602, 1491, 1423, 1274, 1078, 1031, 994, 915, 749, 696, 605, 563. LRMS (rel. int.) m/z 238 (26), 195 (4), 182 (17), 169 (1), 141 (72), 128 (100), 115 (64), 91 (29), 65 (15). Anal. Calcd. for $C_{12}H_{14}Se$: C, 60.76, H, 5.95. Found: C, 61.06, H, 6.08.

1-(methylseleno)-1-tributylstannyl-2-phenylethene (8c): (0.38g, 80%) ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.81 (t, *J*= 6.1 Hz, 9H), 1.1-1.8 (m, 18H), 2.28 (s, 3H), 7.10 (s, 1H), 7.12-7.15 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) 6.0, 11.7, 13.6, 28.9, 126.6, 127.2, 128.1, 137.0, 137.5, 141.6. IR (film) 3076, 3056, 2956, 2924, 2870, 2853, 1484, 1462, 1443, 1418, 1073, 902, 875, 732, 697, 671. LRMS (rel. int.) m/z 433 (8), 429 (29), 327 (82), 271 (63), 215 (97), 231 (100), 121 (58), 102 (85), 77 (22). Anal. Calcd. for $C_{21}H_{36}SeSn$: C, 51.88, H, 7.46. Found: C, 51.77, H, 7.42.

1-(methylseleno)-2-phenylethene (8d): (0.159g, 90%) ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.25 (s, 3H), 6.60 (d, *J*= 15.8 Hz, 1H), 7.11 (d, *J*= 15.8 Hz, 1H), 6.56 (d, *J*= 10.4 Hz, 1H), 6.90 (d, *J*= 10.4 Hz, 1H), 7.2-7.4 (m, 5H), ^{13}C NMR (50 MHz, $CDCl_3$) 5.4, 8.8, 119.9, 121.0, 124.2, 125.5, 126.9, 128.1, 128.2, 128.5, 129.2, 130.2, 137.3, 137.4, 147.3. IR (film) 3056, 3020, 2927, 1598, 1564, 1464, 1444, 1426, 1275, 1029, 914, 875, 773, 761, 731, 698, 676, 566, 514. LRMS (rel. int.) m/z 198 (100), 197 (30), 196 (48), 183 (9), 107 (10), 89 (1), 77 (1). Anal. Calcd. for $C_9H_{10}Se$: C, 55.12, H, 4.63. Found: C, 55.07, H, 5.25.

1-(methylseleno)-1-deutero-2-phenylethene (8e): (0.188g, 98%) ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.25 (s, 3H), 6.59 (t, *J*= 6.2 Hz, 1H), 7.2-7.4 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): 5.3, 8.8, 124.1, 125.4, 126.8, 127.0, 128.0, 128.1, 128.2, 128.5, 129.1, 130.0, 130.1, 134.7, 137.4. IR (film) 3101, 3056, 3020, 2927, 1598, 1564, 1494, 1444, 1426, 1347, 1275, 940, 914, 875, 773, 781, 731, 696, 676, 662, 566, 514. LRMS (rel. int.) m/z 199 (100), 197 (25), 184 (32), 116 (2), 103 (20), 92 (10), 77 (4), 51 (11). Anal. Calcd. for C_9H_9SeD: C, 54.56, H, 5.60. Found: C, 55.07, H, 5.50.

Reaction with $CrCl_2$: Freshly distilled DMF (4 mL) was added during a 10 min period to chromium (II) chloride (0.245 g, 2.0 mmol) under argon atmosphere and magnetic stirring. A solution of 1-iodo-1-(methylseleno)-2-phenylethene (0.323 g; 1.0 mmol) in DMF (2 mL) was then added and the reaction temperature raised to 45 °C. The mixture was stirred for further 2 h at room temperature, and then it was quenched with saturated solution of NH_4Cl, extracted with hexane and washed with brine. After drying with $MgSO_4$ and removing the solvent the residue was purified by flash silica gel chromatography eluting with hexane. Compound **8d** was obtained (0.169 g, 86%).

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