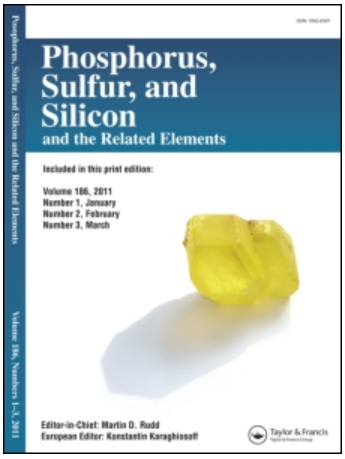


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

NICKEL (II) CATALYZED SUBSTITUTION OF HALOGENS IN 1-HALO-1-CHALCOGENE ALKENES BY CHALCOGENATE ANIONS

Hélio A. Stefani[a]; João V. Comasseto[b]; Nicola Petragnani[b]; Antonio L. Braga[c]; Paulo H. Menezes[a]; Elena V. Gusevskaya[d]
[a] Departamento de Farmaácia, Faculdade de Ciěncias Farmacěuticas, Universidade de São Paulo, São Paulo, SP, Brasil [b] Institute de Química, Universidade de São Paulo, São Paulo, SP, Brasil [c] Departamento de Química, Universidade Federal de Santa Maria, Santa Maria, RS, Brasil [d] Depto. de Química, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil

To cite this Article Stefani, Hélio A. , Comasseto, João V. , Petragnani, Nicola , Braga, Antonio L. , Menezes, Paulo H. and Gusevskaya, Elena V.(1997) 'NICKEL (II) CATALYZED SUBSTITUTION OF HALOGENS IN 1-HALO-1-CHALCOGENE ALKENES BY CHALCOGENATE ANIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 126: 1, 211 — 222
To link to this Article: DOI: 10.1080/10426509708043561
URL: http://dx.doi.org/10.1080/10426509708043561

Phosphorus, Sulfur, and Silicon, 1997, Vol. 126, pp. 211-222
Reprints available directly from the publisher
Photocopying permitted by license only

NICKEL (II) CATALYZED SUBSTITUTION OF HALOGENS IN 1-HALO–1-CHALCOGENE ALKENES BY CHALCOGENATE ANIONS

HÉLIO A. STEFANI[a*], JOÃO V. COMASSETO[c], NICOLA PETRAGNANI[c], ANTONIO L. BRAGA[d], PAULO H. MENEZES and ELENA V. GUSEVSKAYA[b]

[a]*Departamento de Farmácia, Faculdade de Ciências Farmacêuticas, Universidade de São Paulo, Cx. Postal 66083, CEP 05508–900, São Paulo, SP - Brasil.* [b]*Depto. de Química, Universidade Federal de Minas Gerais, 31270–901, Belo Horizonte, MG - Brasil.* [c]*Instituto de Química, Universidade de São Paulo, São Paulo, SP - Brasil.* [d]*Departamento de Química, Universidade Federal de Santa Maria, Santa Maria, RS - Brasil*

(Received 2 July, 1996; In final form 27 February, 1997)

Bis(bipyridine)nickel (II) bromide catalyzes the substitution of chlorine, bromine and iodine in 1-halo–1-chalcogene alkenes [RCH=CX(YR^1), R = C_6H_5, n-C_4H_9; R^1 = CH_3, C_6H_5; X = Cl, Br, I; Y = S, Se] by phenylselenolate and phenyltellurolate anions leading to the S-Se, Se-Te and Se-Se asymmetrically substituted ketene chalcogeneacetals [RCH=C(YR^1)$Y^1C_6H_5$] under mild conditions (30–70°C, 1 atm) and in good yields (80–95%) within a short reaction time (10–60 min). The following compounds were prepared: C_6H_5CH=C($SeCH_3$)SeC_6H_5, C_6H_5CH=C(SCH_3)SeC_6H_5, n-C_4H_9CH =C($SeCH_3$)SeC_6H_5, n-C_4H_9CH=C(SCH_3)SeC_6H_5, n-C_4H_9CH=C(SC_6H_5)SeC_6H_5, n-C_6H_5 CH=C($SeCH_3$) TeC_6H_5.

Keywords: 1-halo–1-chalcogenealkenes; halogen substitution; nickel catalyst; ketene chalcogeneacetals

INTRODUCTION

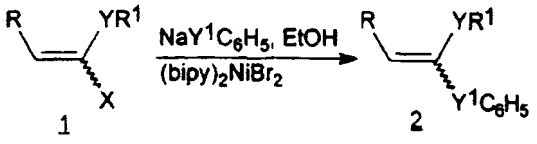
Organoselenium[1] and organotellurium[2,3] compounds are nowadays widely employed in many types of important synthetic operations. Among the organoseleno- and organotelluro compounds with synthetic applications are the vinylic derivatives of these elements[4,5]. However, very little information is available in the literature about the synthetic utility of ketenechalcogeneacetals. To some extent this fact is due to the lack of convenient and efficient methods for their

* Corresponding author.

preparation. In recent years some methods to synthesize ketene selenoacetals were developed[6]. An easy process was described by Cristau et al.[6b], which consists in the substitution of bromine atoms of vinylic 1,1-dibromides by phenylselenolate anions catalyzed by Ni (II) complexes. However, by this method only symmetrically substituted thio- and seleno keteneacetals are available. In this work we extended this methodology to the synthesis of mixed ketene chalcogeneacetals and studied the effect of the reaction variables in order to find the optimum conditions for maximum yields.

RESULTS AND DISCUSSION

In previous works we synthesized 1-halo–1-chalcogene alkenes (1) by addition of hydrogen halides to thio- and selenoacetylenes[7] and by carbocupration of phenylselenoacetylene followed by reaction with a halogen source[8]. In this work it was found that $(bipy)_2NiBr_2$ catalyzes the substitution of chlorine, bromine and iodine in 1 by phenylselenolate or phenyltellurolate anions under mild conditions, leading to ketene chalcogene acetals (2) (Eq. 1, Table 1).



(1)

1a	$R=C_6H_5$; Y=Se; $R^1=CH_3$; X=Br	2a	$R=C_6H_5$; =Se; $R^1=CH_3$; Y^1=Se
1b	$R=C_6H_5$; YY =S; $R^1=CH_3$X=Br	2b	R=; Y=S; $R^1=CH_3$; Y^1=Se
1c	R=n-C_4H_9; Y=Se; $R^1=CH_3$; X=Br	2c	R=n-C_4H_9; Y=Se; $R^1=CH_3$; Y^1=Se
1d	R=n-C_4H_9; Y=S; $R^1=CH_3$; X=Br	2d	R=n-C_4H_9; Y=S; $R^1=CH_3$; Y^1=Se
1e	R=n-C_4H_9; Y=Se; $R^1=CH_3$; X=Cl	2e	$R=C_6H_5$; Y=Se; $R^1=CH_3$; Y^1=Te
1f	R=n-C_4H_9; Y=Se; $R^2=CH_3$; X=I	2f	R=n-C_4H_9; Y=S; $R^1=C_6H_5$; Y^1=Se
1g	$R=C_6H_5$; Y=S; $R^1=CH_3$; X=I		
1h	R=n-C_4H_9; Y=S; R=C_6H_5; X=Br		

The catalytic effect of $(bipy)_2NiBr_2$ is illustrated by the data given in Figure 1 and in Table I.

As can be observed the introduction of the nickel complex leads to a 10–15 fold increase in the reaction rate and improves the yields of the desired products. Thus, in the presence of the catalyst the yield of 1-thiomethyl–1-(selenophenyl)–2-phenylethene (2b) reached 95% at virtually complete conversion of the alkene 1b with excellent selectivity with respect to both alkene and diphenyl diselenide (entry 3, Table 1), whereas in the non-catalytic reaction under the same condi-

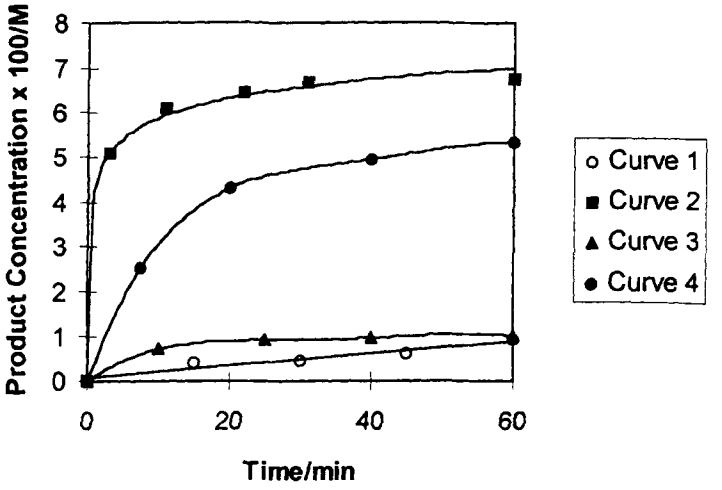


FIGURE 1 Product concentration *vs* reaction time at the non-catalytic (curves 1 and 3) and catalytic (curves 2 and 4) substitution of a bromine atom in $C_6H_5CH{=}CBr(SCH_3)$ (curves 1 and 2, 50^0C) and $n\text{-}C_4H_9CH{=}CBr(SCH_3)$ (; curves 3 and 4, 75^0C) by the phenylselenolate anion. Conditions: [alkene 1b or 1d] = 7×10^{-2}M; $[(C_6H_5Se)_2] = 4.2 \times 10^{-2}$M; $[NaBH_4]=10^{-1}$M $[(bipy)_2NiBr_2] = 3.75 \times 10^{-3}$M; solvent – EtOH.

tions only 12% yield was obtained at 30–40% selectivity (entry 1, Table 1). Similar results were obtained for 1-bromo–1-(thiomethyl)–1-hexene (1d) (entries 8 and 10, Table 1) and for the other examined alkenes (Table 1).

To prevent the decomposition of the nickel complex, excess of sodium borohydride used for generating the phenylselenolate anion must be avoided.The introduction of sodium borohydride into a stirred ethanol solution of diphenyl diselenide must be stopped immediately after the yellow solution turned colorless. It is also essential to add the alkene to the reaction mixture prior to the addition of the catalyst, otherwise a partial deactivation of the catalyst occurs. When the alkene (1) was introduced just 2 min after the addition of $(bipy)_2NiBr_2$ much poorer yields of 2 were achieved.

To find the most favorable conditions for the synthesis of the ketene chalcogeneacetals (2), the reaction was performed at different temperatures and relative amounts of diphenyl diselenide, catalyst and alkene (1a-1d).

TABLE I $(Bipy)_2NiBr_2$ – Catalyzed Reactions of a Halogen Substitution by Chalcogenate Anions in 1-Halo-1-Chalcogene Alkenes

Entry	*Alkene*	*Product*	*Temperature (°C)*	*Catalyst Concentration* $\times 10^3$ *(M)*	*Alkene Concentration* $\times 10^2$ *(M)*	C_S[a] *(%)*	S_S[b] *(%)*	C_{Se}[a] *(%)*	S_{Se}[b] *(%)*	*Yield*[c] *(%)*
1	1b	2b	50	0	7.0	30	40	35	30	12
2	1b	2b	50	1.90	7.0	75	70	60	70	50
3	1b	2b	50	3.75	7.0	100	95	80	100	95
4[e]	1b	2b	50	3.75	7.0	100	95	80	100	95
5	1b	2b	50	7.50	7.0	80	45	50	60	35
6	1b	2b	30	3.75	7.0	50	90	75	50	45
7	1b	2b	50	3.75	3.5	80	60	25	80	50
8	1d	2d	75	0	7.0	20	70	80	15	15
9	1d	2d	75	1.90	7.0	60	90	80	50	55
10	1d	2d	75	3.75	7.0	90	85	90	70	75
11	1d	2d	75	7.50	7.0	90	50	80	50	45
12	1d	2d	50	3.75	7.0	45	70	75	35	30
13	1d	2d	30	3.75	7.0	very slow reaction				~5
14	1d	2d	75	3.75	3.5	90	90	70	50	80
15	1d	2d	75	3.75	10.0	70	70	80	70	50
16[d]	1d	2d	75	1.90	15.0	60	35	100	75	20
17	1a	2a	30	3.75	7.0	85	95	80	90	80
18	1a	2a	50	3.75	7.0	85	95	80	85	80
19	1a	2a	50	3.75	3.5	80	90	60	50	70
20	1c	2c	30	3.75	7.0	55	85	75	50	45
21	1c	2c	50	3.75	7.0	85	90	80	75	75
22[f]	1c	2c	75	3.75	7.0	85	95	80	90	80
23	1e	2c	30	3.75	7.0	65	70	90	45	45
24[g]	1f	2c	reflux	3.75	7.0					80[h]
25[i]	1g	2b	reflux	3.75	7.0					70[h]
26[f,j]	1a	2e	reflux	3.75	7.0					80[h]
27	1h	2f	reflux	3.75	7.0					70[h]

[a] C_S and C_{se} – conversions of alkene and $(SePh)_2$, respectively; [b] S_S and S_{se} – selectivities based on reacted alkene and $(SePh)_2$, respectively.
[c] Yields - based on an initial concentration of the alkene.
[d] Reaction time - 10min. [e] $[NaBH_4] = 5 \times 10^{-2}$M; $[(SePh)_2] = 2.1 \times 10^{-2}$M; [f] Reaction time – 30min. [g] Reaction time – 1.5h [h] Yields of isolated pure products.
[i] Reaction time - 6h [j] $[(TePh)_2] = 4.2 \times 10^{-2}$M.
Conditions: $[NaBH_4] = 10^{-1}$M; $[(SePh)_2] = 4.2 \times 10^{-2}$M; reaction volume – 10mL; solvent - EtOH; reaction time – 1h.

Temperature Effect

The effect of the temperature in the reaction of the bromine substitution is similar for all studied alkenes [Table 1, entries 3, 6 (1b); entries 10, 12, 13 (1d); entries 20–22 (1c)]. The selectivity for product formation based on the reacted alkene is very slightly influenced within 30–75°C, but with rising the temperature up to 75°C the final alkene and diphenyl diselenide conversion, as well as the selectivity for the ketene chalcogeneacetal formation sharply increase for all alkenes, except for the most reactive one (1a). However, at temperatures higher than 40°C the concentration of ketene chalcogeneacetals 2a and 2c after reaching a maximum decreases with reaction time (Figure 2, curves 2' and 4'). In this way, for these reactions the optimization of the reaction time and temperature to achieve the best synthetic results seems to be a problem of special importance.

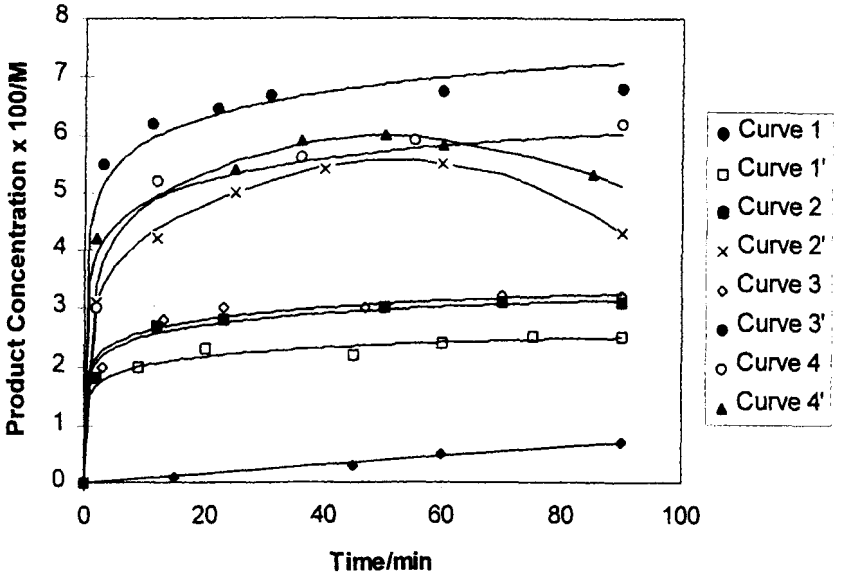


FIGURE 2 Product concentration *vs* reaction time at the catalytic substitution of a bromine atom by the phenylselenolate anion: 1d (curves 1 and 1'); 1c (curves 2 and 2'); 1b (curves 3 and 3'); 1a (curves 4 and 4'). Conditions: [alkene 1a, 1b, 1c, or 1d] = 7×10^{-2} M; $[(C_6H_5Se)_2] = 4.2 \times 10^{-2}$M; $[NaBH_4] = 10^{-1}$ M; $[(bipy)_2NiBr_2] = 3.75 \times 10^{-3}$M; solvent – EtOH; Temperatures: 30°C (curves 1, 2, 3, 4); 50°C (curves 1', 2', 3', 4')

Effect of the Catalyst Concentration

The reaction of the alkenes 1b and 1d with phenylselenolate were carried out at the $(bipy)_2NiBr_2$ concentration in the range of 0.0 - 7.5 x 10^{-3}M [Table 1, entries 2–5 (1b); entries 9–11 (1d)]. With up to 3.75 x 10^{-3} M concentration of the nickel complex, the reaction rates, reagent conversion, total yield of products, and

selectivity for their formation are improved. A further addition of catalyst (up to 7.5 x 10^{-3}M) leads to a sharp decrease in all reaction parameters mentioned above. Selectivity for the vinylic substitution falls down to 45–50%, presumably, due to a side reaction between the catalyst and sodium phenylselenolate[9], which causes the catalyst deactivation. The optimal molar ratio of the catalyst with regard to both alkene and sodium phenylselenolate was found to be about 5 mol % (entries 3 and 10, Table 1). Under these conditions the best selectivity and product yields were achieved with reagent conversions of 85–100%. It should be mentioned that the catalyst concentration produces the most essential effect on the transformation of selenium containing species. Selectivity for the bromine substitution based on reacted diphenyl diselenide decreases with both increase and decrease in the catalyst concentration with respect to the optimal one.

Effect of the Alkene Concentration

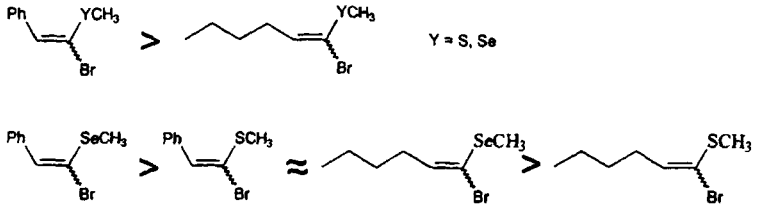
The variation of the initial alkene (1) concentration (other parameters maintained) also revealed that the relative amounts of the components strongly influence the efficiency of the ketene chalcogeneacetal (2) formation [Table 1, entries 3 and 7 (1b); entries 10, 14 and 15 (1d); entries 18, 19(1a)]. In all cases the best results were achieved at a 7.0 x 10^{-2}M concentration of the alkene. The decrease in the alkene concentration to 3.5 x 10^{-2}M concentration causes undesirable changes in the reagent conversion and/or selectivity for the product formation. The decrease in the selectivity based on reacted diphenyl diselenide (S_{Se}) could partially be due to the catalyst deactivation by the selenolate anion mentioned above. A further increase in alkene concentration (higher than 7.0 x 10^{-2}M) causes a decrease in the product yield.

The influence of the relative amounts of the alkene 1d with respect to diphenyl diselenide is illustrated by entries 10, 14–16 in Table 1. The molar ratio between diphenyl diselenide and both sodium borohydride and $(bipy)_2NiBr_2$ were maintained. It can be seen that the molar ratio of the alkene to diphenyl diselenide should be close to the stoichiometric one with a little excess of diphenyl diselenide (entry 10, Table 1).

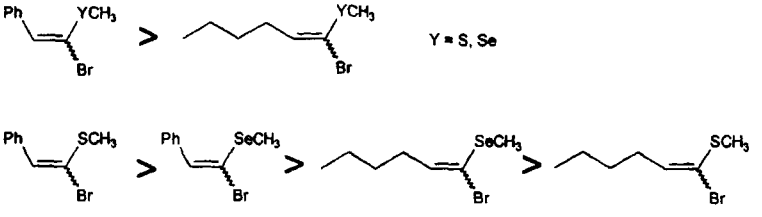
Comparison Between the Reactivity of the 1-Halo–1-Chalcogene Alkenes:

The data on the reactivity of the various 1-halo–1-chalcogene alkenes towards the substitution of bromine by phenylselenolate anion are presented in Table 1 and Figure 2. Reactions were carried out at temperatures of 30°C and 50°C. These conditions are not the optimal ones for the maximum yield, but offer conditions for the comparison between the substrates. Analysis of the yields of the ketene chalcogenoacetals and the kinetic curves of their accumulation revealed the following reactivity order (Scheme 1)

Order of reactivity in the reaction at 30°C:



Order of reactivity in the reaction at 50°C:



SCHEME 1

Stereochemical Aspects

The addition of hydrogen halides to thio- and selenoacetylenes presents a low stereoselectivity, leading to mixtures of the Z and E 1-halo–1-thio- or 1-halo–1-seleno alkenes (1)[7]. The substitution reactions were performed with these mixtures of alkenes, leading to mixtures of the corresponding chalcogeneacetals in isomer ratios similar to those of the starting haloalkenes (1) as demonstrated by GC, ^{1}H NMR and ^{13}C NMR data. This fact suggests that the reaction occurred with retention of the double bond geometry. The assignment of the stereochemistry of tri- and tetra-substituted vinylic derivates of selenium by spectroscopic methods is a matter of controversy[10] and our group is working on the development of secure and general methods to unambiguously assign the geometry of such species containing selenium and tellurium, in order to elucidate the stereochemical outcome of the reaction described in this paper and other reactions in development in our group[11] involving tri- and tetra-substituted alkenes.

Optimum Conditions for Maximum Yield in the Substitution Reaction 1 → 2

Based on the obtained data, the most favorable conditions for the transformation of 1a-1d into 2a-2d were found. After a short reaction time (10–60 min) at mild conditions (30–75°C) the yields of 2 reached 80–95% depending on the parent alkene. Entries 23–27 (Table 1) illustrate some applications of this reaction in the substitution of chlorine, bromine and iodine atoms for phenylselenolate and phenyltellurolate anions. For these reactions the optimal conditions were not determined. In conclusion, the reaction of 1halo–1-chalcogenealkenes with selenolate and tellurolate anions catalyzed by $(bipy)_2NiBr_2$ is an efficient method of synthesis of mixed ketene chalcogenoketene.

EXPERIMENTAL

Analytical Methods

General: ^1H NMR spectra were recorded on a Bruker AC–200 (200MHz) and a Bruker DPX 300 (300MHz) spectrometers with tetramethylsilane as the standard. ^{13}C NMR spectra were obtained on a Bruker AC–200 (50MHz) and a Bruker DPX 300 (75MHz) spectrometers using the central peak of $CDCl_3$ (77.23ppm) as the standard. 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 analyses were performed at the Microanalytical Laboratory of the Institute of Chemistry - USP. The products and starting reagents were analyzed on a Hewlett Packard–5890 chromatograph with a flame-ionization detector using a HP–1 capillary column (5m x 0.53mm × 2.65μm).

Solvents and Reagents

Column chromatography were carried out with Merck silica-gel (230–400 mesh) according to the procedure by Still and coworkers[12]. 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[13]. THF was distilled from sodium/benzophenone under N_2, immediately before use. Selenium metal (320 mesh) and n-BuLi (in hexane solution) were purchased from Aldrich. The remaining chemicals were obtained from commercial sources. All operations were carried out in flame dried glassware, under an inert atmosphere of dry and deoxygenated N_2. Diphenyl diselenide[14], diphenyl ditelluride[15],

seleno- and thioacetylenes[16] were prepared by described methods. 1-Halo–1-seleno alkenes (1a, 1c, 1e and 1f) were prepared according to reference 7. Their analytical data agree with the published ones[7].

1-Halo–1-thio alkenes (1b, 1d, 1g and 1h) were prepared following a procedure similar to that used to prepare the seleno analogs[7].

Addition of Hydrogen Halides to Thioacetylenes – Typical Procedures

In a flask containing the thioacetylene (10.0 mmol) in benzene / acetic acid (3:1; 15.0 mL) at room temperature was added concentrated hydrogen halide [37% HCl, 48% HBr, 57% HI (3.0 mL)]. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by gas chromatography. After all the thioacetylene was consumed, the mixture was dilluted with hexane (50.0 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.

The same procedure was used for the reaction catalyzed by $HgCl_2$ (0.135g; 0.5 mmol) using chloroform (50 mL) as the solvent.

(Z+E)1-Bromo–1-(thiomethyl)–2-phenylethene(1b): Anal.Calcd. for C_9H_9SBr: C, 47.17; H, 3.96. Found: C, 47.50; H, 3.81. 300 MHz ^1H NMR ($CDCl_3$) δ 2.3 (s, 3H); 2.4 (s, 3H); 7.0 (s, 1H); 7.1 (s; 1H); 7.2 (m, 3H); 7.4 (m, 2H). 75.47 MHz ^{13}C NMR ($CDCl_3$) δ 18.6; 19.5; 119.4; 120.8; 127.8; 128.0; 128.4; 128.8; 130.7; 135.5; 137.5. IR (neat) $\nu_{max/cm-1}$: 3021; 2921; 2352; 1590; 1490; 1438; 1075; 920; 876; 749; 692; 552; 517; 509; 497. Mass spectrum (rel.intensity) 228 (27); 149 (58); 134 (100); 115 (29); 102 (10); 89 (62); 69 (14); 63 (10).

(Z+E)1-Bromo–1-(thiomethyl)–1-hexene (1d): Anal.Calcd. for $C_7H_{13}SBr$: C, 40.22; H, 6.22. Found: C, 41.39; H, 6.13. 300 MHz ^1H NMR ($CDCl_3$) δ 0.93 (t, J=7.2 Hz, 3H); 1.35 (m, 4H); 2.20 (m, 2H); 2.34 (s, 3H); 2.36 (s, 3H); 6.18 (t, J=6.98 Hz, 1H); 6.27 (t, J=7.59Hz, 1H). 75.47 MHz ^{13}C NMR ($CDCl_3$) δ 13.4; 18.1; 20.9; 29.0; 30.7; 119.9; 136.5. IR (neat) $\nu_{max/cm-1}$ 2956; 2924; 2861; 1443; 843; 500; 484; 476; 459; 441. Mass spectrum (EI) (rel.intensity) 210 (4); 193 (3); 167 (18); 153 (1); 129 (30); 123 (1); 113 (1); 97 (2); 87 (42); 81 (100); 71 (38); 59 (1).

(Z+E)1-Iodo–1-(thiomethyl)–2-phenylethene(1g): Anal. Calcd. For C_9H_9SI: C, 39.14; H, 3.28. Found: C, 39.49 ; H, 3.36. 300 MHz ^1H NMR ($CDCl_3$) δ 2.2 (s, 3H); 2.3 (s, 3H); 6.9 (s, 1H); 7.2 (m, 3H); 7.4 (m, 2H); 7.6 (s, 1H). 75.47 MHz ^{13}C NMR ($CDCl_3$) δ 21.2; 24.1; 94.6; 95.4; 127.8; 128.1; 128.3; 128.5; 129.0; 134.5; 137.0; 137.8; 145.3. IR(neat) $\nu_{max/cm-1}$: 3054; 3022; 2916; 1582; 1488;

1442; 1430; 1313; 1074; 1029; 967; 919; 866; 748; 693; 592; 512; 502; 493. Mass spectrum (rel.intensity) 276 (14); 148 (19); 134 (100); 89 (34); 63 (13).

(Z+E)1-Bromo–1-(thiophenyl)–1-hexene – Anal. Calcd. For $C_{12}H_{15}SBr$: C, 53.14; H, 5.57. Found: C, 53.51; H, 5.72. 300 MHz ^1H NMR ($CDCl_3$) δ 0.9 (t, J=7.0 Hz, 3H); 1.3 (m, 4H); 2.2 (m, 2H); 2.6 (m, 2H); 6.48 (t, J=7.04 Hz, 1H); 6.55 (t, J=7.01 Hz, 1H); 7.2 (m, 5H). 75.47 MHz ^{13}C NMR ($CDCl_3$) δ 14.4; 22.2; 30.2; 39.6; 116.8; 125.2; 128.1; 129.5; 129.7; 130.0; 137.7; 144.1. IR (neat) $\nu_{max/cm-1}$: 3064; 2956; 2927; 2862; 1582; 1477; 1440; 1378; 1068; 1024; 842; 739; 688; 533. Mass spectrum (rel.intensity) 272 (13); 227 (9); 191 (13); 190 (7); 147 (51); 115 (25); 91 (100); 71 (31).

Vinylic Substitution Reactions - Typical Procedure

The reactions were carried out in a magnetically stirred reactor equipped with a condenser and a sampling system. A mixture of diphenyl diselenide (0.131g, 0.42mmol) and sodium borohydride (0.028g, 0.75mmol) was placed in the reactor. The reactor was purged with nitrogen and ethanol (8mL) was injected via syringe to the stirred mixture at room temperature. Then a solution of sodium borohydride (0.01g, 0.25mmol) in ethanol (2mL) was introduced into the system via syringe until the yellow color of the solution faded. To this stirred solution 1-bromo–1-thiomethyl–1-hexene (0.148g, 0.7mmol) and $(bipy)_2NiBr_2$ (0.02g, 0.0375mmol) were added in turns at 70°C. The progress of the reaction was monitored by gas chromatography. The reaction mixture was stirred for the time reported in notes of Table I. The reaction conditions and amounts of catalyst and reagents for all experiments are mentioned in Table 1. Ketene chalcogeneacetals were separated from the reaction mixture by addition of water and extraction with ether. The organic phase was dried with $MgSO_4$ and the solvents were evaporated under vacuum. The resulting yellow oils were purified by flash SiO_2 column chromatography using hexane as the eluent. For yields and reaction times see Table 1.

(Z+E) 1-selenophenyl–1-(selenomethyl)–2-phenylethene (2a) (ratio of geometric isomers: 2:1): Anal.Calcd for $C_{15}H_{14}Se_2$:C, 51.14; H, 3.98. Found: C, 51,17; H, 3,97. 200 MHz ^1H NMR ($CDCl_3$) for major isomer: δ 7.57 –7.14 (m, 11H), 2.13(s, 3H); for minor isomer: 7.14–7.57, 2.19 (s; 3H); δ 50 MHz ^{13}C NMR ($CDCl_3$) for major isomer: δ 10.55, 122.10, 127.37, 127.49, 128.07, 128.77, 129.28, 131.68, 132.12, 137.29, 139.85; for minor isomer: 9.80, 121.46, 127.34, 127.44, 128.02, 128.62, 128.91, 130.49, 132.75, 135.34, 137.36. IR (neat) $\nu_{max/cm-1}$ 1000 (m), 1022 (w), 1069 (m). Mass spectrum (EI) m/z (rel. intensity) 354 (42), 259 (11), 197 (46), 182 (49), 157 (15), 116 (73), 102 (100), 77 (66).

(Z+E) 1-Thiomethyl–1-(selenophenyl)–2-phenylethene (2b): (ratio of geometric isomers: 1.5:1): Anal. Calcd for $C_{15}H_{14}SSe$: C, 59.02; H, 4.59. Found: C, 59,32; H, 4.82. 200 MHz ^1H NMR ($CDCl_3$) for major isomer: δ 7.91 - 7.54 (m, 11H), 2.62 (s, 3H); for minor isomer: 7.91–7.54 (m, 11H), 2.67 (s, 3H). 50 MHz ^{13}C NMR ($CDCl_3$) for major isomer: δ 19.28, 127.23, 127.50, 128.04, 128.80, 129.26, 130.61, 131.76, 132.08, 137.02, 138.39; for minor isomer:18.29, 127.20, 127.50, 128.04, 128.80, 128.98, 130.61, 131.15, 132.51, 136.50, 137.02. IR (neat) $\nu_{max/cm-1}$.1000(m), 1022 (w), 1068 (m). Mass spectrum (EI) m/z (rel. intensity) 306 (13), 157 (5), 149 (85), 134 (100), 116 (26), 102 (11), 89 (15), 77 (13).

(Z+E) 1-Selenophenyl–1-(selenomethyl)–1-hexene (2c): (ratio of geometric isomers: 2:1): Anal. Calcd for $C_{13}H_{18}Se_2$: C, 46.99; H, 5.42. Found: C, 47.23; H, 5.32. 200 MHz ^1H NMR ($CDCl_3$) for major isomer: δ 7.48 - 7.41 (m, 2H), 7.29 - 7.21 (m, 3H), 6.46 (t, J=7 Hz, 1H), 2.39–2.24 (m, 2H), 2.10 (s, 3H), 1.45–1.25 (m, 4H), 0.94–0.84 (m, 3H); for minor isomer: 7.48 - 7.41 (m, 2H), 7.29 - 7.21 (m, 3H), 6.29 (t, J=7.0Hz, 1H), 2.39–2.24 (m,2H), 2.12 (s, 3H), 1.45–1.25 (m, 4H), 0.94–0.84 (m, 3H). 50 MHz ^{13}C NMR ($CDCl_3$) for major isomer: δ 9.26, 13.87, 22.20, 31.18, 32.93, 116.25, 126.86, 129.06, 131.36, 145.51; for minor isomer: 9.05, 13.87, 22.20, 30.91, 33.18, 117.54, 126.73, 128.97, 131.42, 141.53. IR (neat) $\nu_{max/cm-1}$ .1000 (m), 1022 (w), 1068 (m). Mass spectrum (EI) m/z (rel. intensity) 334 (51), 157 (19), 135 (39), 116 (24), 81 (100), 77 (25).

1-Thiomethyl–1-(selenophenyl)–1-hexene (2d) (starting from a single isomer of 1d, a single isomer of 2d was obtained): Anal. Calcd for $C_{13}H_{18}SSe$: C, 54.74; H, 6.32. Found: C, 55.07; H, 6.00. 200 MHz ^1H NMR ($CDCl_3$) δ 7.49 - 7.42 (m, 2H), 7.31 - 7.20 (m, 3H), 6.34 (t, J=7 Hz, 1H), 2.41 - 2.23 (m, 2H), 2.21 (s, 3H), 1.51 - 1.25 (m, 4H), 0.91 (t, J=7.4 Hz, 3H). 50 MHz ^{13}C NMR ($CDCl_3$) 13.87, 18.30, 22.26, 31.02, 32.02, 126.02, 126.86, 129.03, 131.30, 131.45, 144.61. IR (neat) $\nu_{max/cm-1}$:1000 (m), 1023 (w), 1069 (w). Mass spectrum (EI) m/z (rel. intensity) 286 (19), 157 (5), 129 (20), 87 (100), 81 (93), 77 (12).

(Z+E) 1-Selenomethyl–1-(telurophenyl)–2-phenylethene (2e): (ratio of geometric isomers: 1.5:1): Anal. Calcd for $C_{13}H_{18}SeTe$: C, 41.01; H, 4.73. Found: C, 41.32; H, 4.97. 200 MHz ^1H NMR ($CDCl_3$) δ 7.81 - 7.19 (m, 11H), [2.20 (s); 2.13 (s), 3H]. 50 MHz ^{13}C NMR ($CDCl_3$) for major isomer: δ 14.35, 116.70, 127.49, 128.03, 128.16, 128.73, 129.58, 137.43, 139.72, 146.12; for minor isomer: δ 10.96, 106.07, 127.34, 128.00, 128.16, 128.73, 129.05, 136.52, 138.59, 139.56. IR (neat) $\nu_{max/cm-1}$:1000 (m), 1023 (w), 1068 (m). Mass spectrum (EI) m/z (rel. intensity) 400 (9), 197 (13), 182 (5), 116 (86), 102 (100), 77 (88).

(Z+E) 1-Thiophenyl-1-(selenophenyl)-1-hexene (2f): (ratio of geometric isomers: 1.7:1): Anal. Calcd for $C_{17}H_{20}SSe$: C, 62.26; H, 5.76. Found: C, 62.15; H, 5.82. 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.43 - 7.16 (m, 10H), [6.43 (t, J=7.7 Hz); 6.38 (t, J=7.3 Hz), 1H], 2.42 - 2.30 (m, 2H), 1.45 - 1.23 (m, 4H), 0.91 - 0.82 (m, 3H). 50 MHz ^{13}C NMR ($CDCl_3$) for major isomer: δ 13.88, 22.27, 31.45, 32.79, 123.37, 126.98, 127.63, 128.75, 129.00, 129.68, 131.16, 133.78, 135.32, 146.63; for minor isomer: δ 13.88, 22.30, 31.09, 32.79, 124.80, 126.45, 127.18, 128.68, 128.75, 130.41, 130.74, 133.02, 135.24, 144.57. IR (neat) $\nu_{max/cm-1}$: 1000 (m), 1023 (m), 1068 (m). Mass spectrum (EI) m/z (rel. intensity) 348 (22), 191 (24), 149 (64), 81 (100), 77 (21).

Acknowledgements

The authors thank the following agencies for support: CNPq, GTZ, FAPESP 94/1250–8.

References

[1] C. Paulmier, *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon Press, Oxford, 1986.
[2] (a) N. Petragnani and J. V. Comasseto, *Synthesis*, 793 (1991).(b) N. Petragnani and J. V. Comasseto, *Synthesis*, 897 (1991).
[3] N. Petragnani, *Tellurium in Organic Synthesis*, Academic Press, London, 1994.
[4] J. V. Comasseto, *J. Organometal. Chem.* **253,** 131 (1983).
[5] J. V. Comasseto, *Rev. Heteroatom. Chem.*, **9,** 61 (1993).
[6] (a) W. C. Shin, K. Lee and D. Y. Oh, *Tetrahedron Lett.*, **33,** 5375 (1992). (b) H. J. Cristau, B. Chabaud, R. Labaudiniere and H. Christol, *J. Org. Chem.*, **51,** 875 (1986).(c) J. N. Denis and A. Krief, *Tetrahedron Lett.*, **33,** 3407 (1982).(d) B.T. Gröbel and D. Seebach, *Chem. Ber.*, **110** 852 (1977).
[7] (a) A. L. Braga, PhD Thesis, Universidade de São Paulo, 1989. (b) J.V.Comasseto, P.H. Menezes, H.A. Stefani, G. Zeni and A.L. Braga, *Tetrahedron*, **52,** 9787 (1996).
[8] A.L. Braga, A. Reckziegel, C.C. Silveira and J.V. Comasseto, *Synth. Commun.*, **24,** 1165 (1994).
[9] J. Cristau, B. Chabaud, R. Labaudiniere and H. Christol, *Organometallics*, **4,** 657 (1985).
[10] T.Fäcke, R. Wagner and S. Berger, *J. Org. Chem.*, **58,** 5475 (1993).
[11] (a) H.A. Stefani, I.P. Arruda Campos, L.C. Roque and A.L. Braga, *J. Chem. Res.* (s), 112 (1994). (b) I.P. Arruda Campos, H.A. Stefani, L.C. Roque M.A. Montoro and A.L. Braga, *J. Chem Res.* (s), 112 (1995). (c) I.P. Arruda Campos and H.A. Stefani, *Phophorus, Sulfur and Silicon*, **105,** 73 (1995).
[12] W.C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, **43,** 2923 (1978).
[13] D.D. Perrin W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1966.
[14] H.J. Reich, M.L. Cohen and P.S. Clark, *Org. Synth.*, **59,** 141 (1979).
[15] N. Petragnani, *Tetrahedron*, **11,** 15 (1960).
[16] A.L. Braga, C.C. Silveira, A. Reckziegel and P.H. Menezes, *Tetrahedron Lett.*, **34,** 8041 (1993) and references therein