(S)-N-Methyl-1-(p-methoxybenzyl)-1,2,3,4,5,6,7,8-octahydroisoquinoline (19a). A solution of 0.094 g (0.36 mmol) of the (S)-1-(p-methoxybenzyl)-1,2,3,4,5,6,7,8-octahydroisoquinoline (**16a**) in 2 mL of ethyl formate was heated at 40 °C for 15 h. The reaction mixture was concentrated in vacuo, and the crude formamide was dissolved in 5 mL of diethyl ether to which 0.035 g (0.92 mmol) of lithium aluminum hydride was added. After 2 h of stirring at room temperature, the reaction was quenched successively with 5 drops of water, 3 drops of 20% aqueous KOH solution, and 5 drops of water. The solution was filtered and concentrated, and the crude product was subjected to bulb-to-bulb distillation (0.05 mmHg; 110 °C), which afforded 0.088 g (89%) of the product as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.75 (1 OH, m), 2.36 (3 H, s), 2.50 (1 H, m), 2.77 (2 H, m), 2.90 (2 H, m), 3.77 (3 H, s), 6.80 (2 H, d, J = 8.7 Hz), 7.16 (2 H, d, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 22.9, 23.2, 28.1, 28.2, 30.1, 35.7, 42.8, 47.3, 55.0, 66.2, 113.2, 127.0, 129.1, 129.8, 132.9, 157.3; $[\alpha]^{24}_D$ -76.9° (c 2.9, ether), lit.[11] $[\alpha]^{25}_D$ -78.9° (c 3.0, ether).

Dextrorphan [(+)-3-Hydroxy-17-methylmorphinan] (4a). A solution of 0.139 g (0.51 mmol) of **19a** in 1 mL of phosphoric acid was heated[12] at 135-140 °C for 65 h under argon. The mixture was poured over ice and neutralized with concentrated ammonium hydroxide. Extraction with benzene-ether, drying (K_2CO_3), and concentration in vacuo gave a crude product which was purified via radial chromatography; silica gel, 1 mm thickness, eluted with hexane-triethylamine-ethyl acetate (60:15:25), to give 0.060 g (45%), mp 188-190 °C: $[\alpha]^{24}_D$ +54.0° (c 3.0, ethanol). An authentic sample[13] showed $[\alpha]_D$ +56.3° (c 3.0, ethanol), mp 191-193 °C.

(13) We thank Dr. John Scott, Hofmann-LaRoche for a sample. Previous preparation of (+)-**4a** has been described: Schnider, O.; Grussner, A. *Helv. Chim. Acta* **1951**, *34*, 2211.

(S)-1-Benzyl-1,2,3,4,5,6,7,8-octahydroisoquinoline (16b). In a manner analagous to the preparation of **16a**, **16b** was obtained in 82% yield and HPLC analysis of its naphthamide showed that the enantiomeric excess was 99 ± 1%. The product **16b** was obtained as an oil, via vulb-to-bulb distillation (135 °C, 0.05 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.7 (5 H, m), 1.9 (6 H, m), 2.8 (3 H, m), 3.2 (2 H, m), 7.3 (5 H, br s).

(S)-N-Methyl-1-benzyl-1,2,3,4,5,6,7,8-octahydroisoquinoline (19b). In a manner analogous to **19a**, **19b** was methylated in 82% yield to give an oil, purified by bulb-to-bulb distillation (135 °C, 0.05 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.58 (4 H, m), 1.87 (6 H, m), 2.35 (3 H, s) 2.57 (1 H, t, J = 5 Hz), 2.84 (4 H, m), 7.23 (5 H, m); $[\alpha]^{24}_D$ +9.9° (c 2.87, ethanol).

Morphinan 4b. In a manner similar to the formation of **4a**, the octahydroisoquinoline **19b** was heated in phosphoric acid to give **4b** in 57% yield. The product was purified with radial chromatography using conditons identical with that employed for **4a**: ^{1}H NMR ($CDCl_3$) δ 1.34 (7 H, m), 1.70 (3 H, m), 2.05 (1 H, d of t, J = 2.5, 12.2 Hz), 2.39 (3 H, s), 2.40 (2 H, m), 2.63 1 H, dd, J = 5.6, 18.3 Hz), 2.80 (1 H, br m), 3.03 (1 H, d, J = 18.3 Hz), 7.15 (3 H, m), 7.24 (1 H, d, J = 7.6 Hz); $[\alpha]^{24}_D$ +56.9° (c 1.50, ethanol). reported for the (-)-antipode, $[\alpha]^{25}_D$ -56° (ethanol), mp 33-34 °C.[14] **4b** was obtained as an oil, which did not crystallize.

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Synthesis of Vinyl Selenides or Sulfides and Ketene Selenoacetals or Thioacetals by Nickel(II) Vinylation of Sodium Benzeneselenolate or Benzenethiolate

H. J. Cristau,* B. Chabaud,* R. Labaudiniere, and H. Christol

Laboratoire de Chimie Organique (U.A. 458), ENSCM, F-34075 Montpellier Cêdex, France

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The substitution of a bromine atom on a double bond by benzeneselenolate or benzenethiolate anions is catalyzed by the bis(bipyridine)nickel(II) bromide complex. Various alkenyl selenides or sulfides and seleno- or thioacetals are prepared in good to excellent yields.

A number of useful functional group transformations can be achieved with vinyl selenides or sulfides. Owing to their ability to stabilize carbanionic intermediates for further functionalization and/or the easy removal of the metalloid, they have been widely used in organic synthesis. As a matter of fact, their preparations have held attention these past years, and several methods have been proposed. The preparations of vinyl senelides generally imply multiple steps procedures involving addition of electrophilic selenium on triple or double bonds followed by elimination reactions[1] or Wittig-type reactions with α-selenated ylides.[1f,2] Other possible preparations are the reaction of phosphorus tetraiodide or triiodide with selenoacetals or seleno esters,[1f] the reduction of phenylselenoalkynes,[1d] the reaction of alkynyl trialkyl borates,[1e] alkenylboranes, and alkenyl mercurials,[1d] selenyl halides, or diaryl selenides, the addition of selenic acids[1f,3] and selenols[4] on alkynes, and the syn elimination of selenoacetals monoselenoxides.[5] Vinyl sulfides are obtained by Wittig reaction[6] or addition of a thiolate on a triple bond.[7] Ketene thioacetals are prepared by Wittig,[8] Wittig-Horner,[9] and Peterson[10] re-

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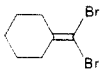
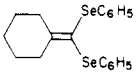
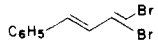
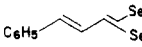
Table I. Vinyl Selenides

case	vinyl bromide[a]	catalyst, mol %	reacn time, h	temp,[b] °C	vinyl selenide	yield,[c] %
1	$CH_3CH{=}CHBrCH_3$	10	6	120	$CH_3CH{=}CH(SeC_6H_5)CH_3$	73
2	$CH_3CH{=}CHBr$	10	6	120	$CH_3CH{=}CHBr$	76
3	$C_6H_5CH{=}CHBr$	10	3	reflux	$C_6H_5CH{=}CHSeC_6H_5$	89
4	$BrCH{=}CHBr$	10	3	120	$BrCH{=}CHSeC_6H_5$	42
					$C_6H_5SeCH{=}CHSeC_6H_5$	26
5	$BrCH{=}CHBr$	20	3	reflux	$C_6H_5SeCH{=}CHSeC_6H_5$	70
6	$C_6H_5CH{=}CBr_2$	20	3	reflux	$C_6H_5CH{=}C(SeC_6H_5)_2$	88
7		20	3	reflux		82
8	$CH_3(CH_2)_5CH{=}CBr_2$	20	3	reflux	$CH_3(CH_2)_5CH{=}C(SeC_6H_5)_2$	73
9		20	3	reflux		89

[a] Reaction done with 3 equiv of vinyl bromide in cases 1, 2, 4 and 1 equiv in case 3 and 2.4 equiv of phenyl selenolate in cases 5–8. [b] Solvent of reaction ethanol. [c] Yield of isolated pure compounds.

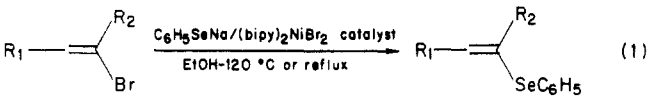
actions or from dithioic acid dianions.[11] To our knowledge, no preparations have been described in the case of vinyl selenides by the direct substitution of halogens on a vinyl halide by a selenolate. Only few of them have been developed for he vinyl sulfides when the substrate is activated by electron-withdrawing groups[12] on the double bond by a solvent like HMPA[13] or with limited success by a transition-metal catalysis.[14]

The method proposed here comes from our first observation that nickel(II) complexes with unsaturated nitrogen heterocycles as ligands catalyze the nucleophilic substitution of an halogen (e.g., bromide, iodide) on an aryl ring by a thiolate or a selenolate.[15]

Results and Discussion

The best catalyst for both syntheses of vinyl sulfides or selenides was found to be, as in the case of aryl derivatives, the bis(bipyridine)nickel(II) bromide.[15]

Synthesis of Vinyl Selenides and Ketene Selenoacetals. The first study done on 2-bromo-2-butene using equimolecular amounts of reagents and 10 mol % of catalyst gave, however, a modest yield of 25% of the corresponding phenyl vinyl selenide. Byproducts isolated from the reaction were diphenyl selenide and bipyridine, depicting the same deactivation already observed in the reaction with aryl halides.[15] This drawback was overcome by using 3 equiv of bromo olefin (Table I, case 1) and applied also to 2-bromo-2-propane (Table I, case 2), which represents in this study the second example of the less reactive olefins (i.e., olefins substituted by electron-donating substituents) (reaction 1).



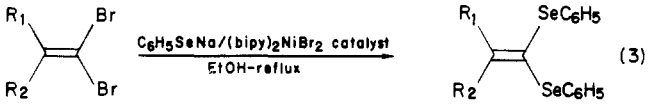
(1)

1, $R_1 = R_2 = CH_3$
2, $R_1 = CH_3$; $R_2 = H$
3, $R_1 = C_6H_5$; $R_2 = H$

In these conditions the phenyl vinyl selenide is obtained in good yields. The other bromo olefins, β-bromostyrene, and 1,2-dibromo and 1,1-dibromo olefins have a better reactivity, and their reaction does not need a large excess of reagent (Table I, cases 3–8). All of them are done with stoichiometric or close to stoichiometric amounts of bromo olefin in milder conditions. In the particular case of substitution on dibromo olefins, one could isolate the monoselenated compound only in the case of 1,2-dibromoethylene together with the diselenated one (Table I, case 4) (reaction 2).

$$BrCH{=}CHBr \xrightarrow[\text{EtOH—120 °C}]{C_6H_5SeNa/(bipy)_2NiBr_2\ \text{catalyst}} \underset{\mathbf{4}}{C_6H_5SeCH{=}CHBr} + \underset{\mathbf{5}}{C_6H_5SeCH{=}CHSeC_6H_5} \quad (2)$$

In all cases of *gem*-dibromo olefins and whatever the conditions used were, one never could characterize the monosubstituted compound (Table I, cases 6–9) (reaction 3).



(3)

6, $R_1 = C_6H_5$; $R_2 = H$
7, $R_1R_2 = (CH_2)_5$
8, $R_1 = n$-hexyl; $R_2 = H$
9, $R_1 = C_6H_5CH{=}CH$; $R_2 = H$

The disubstituted compound was the only product obtained in variable amounts depending on the conditions used. Our method brings an improvement for the preparations of these compounds in comparison to the others which present difficulties in the isolation of pure products,[15] in their generalization,[1f] or in the yields of isolated pure compounds.[1f]

One can see from Table I that the reaction is regioselective in all the investigated cases. Variable results have been, however, obtained concerning the stereoselectivity (Table II). If the reaction seems to be entirely stereospecific either for the *E* or for the *Z* isomers in cases 1, 2, and 4, a partial isomerization affects the selenide obtained from a pure (*Z*)-2-bromovinyl phenyl selenide (case 3).

Synthesis of Vinyl Sulfides and Ketene Thioacetals. The preparation of vinyl sulfides using $(bipy)_2NiBr_2$ as catalyst is not affected by the deactivation of the latter, and the reaction can be performed with smaller amounts of nickel complex. However, contrary to selenides, protic solvents like ethanol or diethylene glycol cannot be used. Several byproducts are present at the end of the reaction together with the desired vinyl sulfide in low yield. These products come from complex processes

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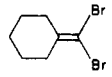
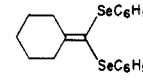
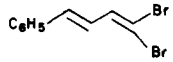
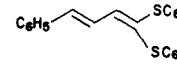
Table II. Stereochemical Results in the Preparation of Some Vinyl Selenides

case	substrate (E/Z)[b]	reacn conditions[a]	vinyl selenide (E/Z)[b]
1	$BrCH{=}CHC_6H_5$ (90/10)	10 mol % $(bipy)_2NiBr_2$ EtOH, 3 h, reflux	$C_6H_5CH{=}CHSeC_6H_5$ (94/6)
2	$BrCH{=}CHSeC_6H_5$	10 mol % $(bipy)_2NiBr_2$ EtOH, 3 h, reflux	$C_6H_5SeCH{=}CHSeC_6H_5$ (>95/5)
3	$BrCH{=}CHSeC_6H_5$ (pure Z)	31 % mol $(bipy)_2NiBr_2$ EtOH, 16 h, reflux	$C_6H_5SeCH{=}CHSeC_6H_5$ (15/85)
4	$CH_3CH{=}CBrCH_3$ (88/12)	120 mol % $(bipy)_2NiBr_2$ EtOH, 24 h, 120 °C	$CH_3CH{=}(SeC_6H_5)CH_3$ (87/13)

[a] Reactions conditions were such that all the starting vinyl bromide was consumed in order to eliminate the influence of the result of the kinetic competition between the two isomers in their reaction with phenyl selenoate. [b] Determined by GC analysis of the mixture using a 5 ft × 0.125 in. stainless steel column packed with 10% SE 30 on WHMDS.

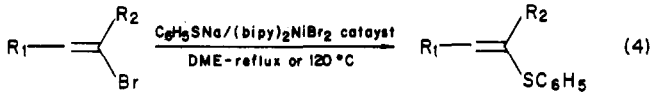
Table III. Vinyl Sulfides

case	vinyl bromide[a]	catalyst, mol %	solvent	temp, °C	reacn time, h	vinyl sulfide	yield,[b] %
1	$CH_3CH{=}CBrCH_3$	3	DME	120	48	$CH_3CH{=}C(SC_6H_5)CH_3$	81
2	$CH_3CH{=}CHBr$	3	DME	120	48	$CH_3CH{=}CHSC_6H_5$	77
3	$C_6H_5CH{=}CHBr$	1	DME	reflux	24	$C_6H_5CH{=}CHSC_6H_5$	75
4	$C_6H_5SeCH{=}CHBr$	1	DME	reflux	24	$C_6H_5SeCH{=}CHSC_6H_5$	89
5	$BrCH{=}CHBr$	2	DME	reflux	24	$C_6H_5SCH{=}CHSC_6H_5$	71
6	$C_6H_5CH{=}CBr_2$	2	toluene	reflux	22	$C_6H_5CH{=}C(SC_6H_5)_2$	85
7		2	toluene	reflux	36		73
8	$CH_3(CH_2)_5CH{=}CBr_2$	2	toluene	reflux	116	$CH_3(CH_2)_5CH{=}C(SC_6H_5)_2$	63
9		2	toluene	reflux	24		78

[a] Reaction done with 1.2 equiv of $C_6H_5S^-$ in cases 1–4 and 2.4 equiv in cases 5–9. [b] Optimum yield of isolated pure compound obtained after the total disappearance of the starting vinyl bromide.

involving the thiolate, the vinyl bromide, and the solvent where, as we could demonstrate, no nickel catalysis is necessary.

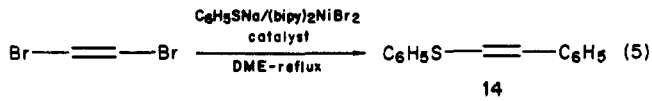
In aprotic solvents like dimethoxyethane or toluene, the side reactions are not observed anymore, and good yields of the desired sulfides are obtained. In these conditions the reaction can be performed even with deactivated vinyl bromides (Table III, cases 1, 2) (reaction 4).



(4)

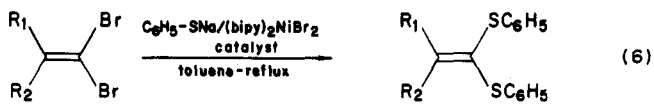
10, R_1 = CH_3; R_2 = CH_3
11, R_1 = CH_3; R_2 = H
12, R_1 = C_6H_5; R_2 = H
13, R_1 = C_6H_5Se; R_2 = H

Analagous conditions allow for the disubstitution of either 1,2-dibromoethylene (Table III, case 5) (reaction 5) or 1,1-dibromoethylenic compounds (Table III, cases 6–9) (reaction 6).



(5)

14



(6)

15, R_1 = C_6H_5; R_2 = H
16, R_1, R_2 = $(CH_2)_5$
17; R_1 = n-hexyl; R_2 = H
18, R_1 = $C_6H_5CH{=}CH$; R_2 = H

For the latter, and contrary to palladium(0),[13a] nickel(II) catalyzes in good yields the regiospecific disubstitution of bromine atoms by thiolate to give the corresponding ketene thioacetals.

The reaction has variable stereochemical results and in most of the cases considered no clear stereochemical relation was observed (Table IV).

In conclusion the $(bipy)_2NiBr_2$ catalysis of the nucleophilic substitution of monobromo- and dibromovinyl derivatives by benzeneselenolate and benzenethiolate allows for an easy preparation of vinyl selenides, vinyl sulfides, and ketene selenoacetals and thioacetals.

Experimental Section

The preparation of $(bipy)_2NiBr_2$ has been already described.[15] Preparations of vinyl selenides and ketene selenoacetals were conducted under an inert atmosphere of N_2, which was not, however, necessary for the workup of reaction mixtures. Preparation of vinyl sulfides and ketene thioacetals did not need an inert atmosphere. Melting points are uncorrected and were measured on an automatic Mettler FP 51 melting point apparatus (heating rate, 2 °C/min). Infrared spectra were recorded on a Perkin-Elmer Model 221 spectrophotometer by using samples as films between KBr disks or as solutions in KBr. Three bands stable in frequency were observed in the range 1000–1070 cm^{-1} for either sulfides or selenides. They may be assigned to the C_6H_5S or C_6H_5Se groups. ^1H NMR spectra were measured in $CDCl_3$ or CCl_4 with a Varian EM-360 L spectrometer with Me_4Si as internal standard. Satellite bands due to ^{77}Se–H couplings have not been taken into account for the analysis of NMR spectra.

Diphenyl diselenide and monobromoalkenes were purchased from Aldrich or Fluka. The latter were used after passing on a short plug of neutral alumina. β,β-Dibromostyrene, 1,1-dibromo-1-nonene, and 1,1-dibromo-4-phenyl-1,3-butadiene were prepared according to the procedure of E. J. Corey and Fuchs.[17] 1,1-(Dibromomethylidene)cyclohexane was prepared according

(17) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769.

Table IV. Stereochemical Results in the Preparation of Some Vinyl Sulfides

case	substrate (E/Z)[b]	reacn conditions[a]	vinyl sulfide (E/Z)[b]
1	$CH_3CH{=}CBrCH_3$ (88/12)	3 mol % $(bipy)_2NiBr_2$ DME, 48 h, 120 °C	$CH_3CH{=}C(SC_6H_5)CH_3$ (56/44)
2	$C_6H_5CH{=}CHBr$ (90/10)	1 mol % $(bipy)_2NiBr_2$ DME, 24 h, reflux	$C_6H_5CH{=}CHSC_6H_5$ (E, 100%)
3	$C_6H_5SeCH{=}CHBr$ (95/5)	1 mol % $(bipy)_2NiBr_2$ DME, 24 h, reflux	$C_6H_5SeCH{=}CHSC_6H_5$ (52/48)

[a] See note *a* in Table II. [b] See note *b* in Table II.

to the procedure of G. H. Posner et al.[18]

Synthesis of Vinyl Selenides and Ketene Selenoacetals. All reactions were conducted in ethanol using sodium phenylselenolate prepared by reduction in this solvent of diphenyl diselenide by sodium borohydride according to the procedure of K. B. Sharpless and Lauser.[19] The reaction conditions and amounts of catalyst and reagents for each case are indicated in Table I. The reactions that needed a temperature of 120 °C were conducted in sealed tubes. The reaction mixtures were diluted with ether (80 mL), washed with water (30 mL) three times, dried (Na_2SO_4), and concentrated in vacuo. The crude mixtures were purified by short-path chromatography on silica (elution hexane) and either Kugelrhor distilled or recrystallized.

2-(Phenylseleno)-2-butene (1): yellow oil (E/Z, 70/30); IR 1061 (m), 1018 (F), 997 (m) cm^{-1}; NMR δ 7.65–7.1 (m, 5 H, C_6H_5), 6.3–5.68 (q, 1 H, J = 8 Hz, =CH), 2.00 (s, 3 H), 1.86 (d, 2.1 H, J = 8 Hz, CH_3, E isomer), 1.60 (d, 0.9 H, J = 8 Hz, Z isomer). Anal. Calcd for $C_{10}H_{12}Se$: C, 56.88; H, 5.73. Found: C, 57.17; H, 5.87.

1-(Phenylseleno)propene (2): yellow oil (E/Z, 55/45); IR 1067 (m) 1020 (F), 998 (m) cm^{-1}; NMR δ 7.72–7.08 (m, 5 H, C_6H_5), 6.68–5.4 (m, 2 H, CH=CH), 1.86 (s, 1.65 H, Z isomer), 1.76 (d, 1.35 H, J = 1.5 Hz, E isomer).

β-(Phenylseleno)styrene (3): yellow oil (E/Z, 96:4); IR [compatible with the literature[1d]] 1068 (m), 1020 (F), 998 (m) cm^{-1}; NMR δ isomer] [E 7.09 (A), 6.79 (B) (J_{AB} = 16.1 Hz) [Z isomer] 6.90 (A), 6.70 (B), (J_{AB} = 10.4 Hz).

2-(Phenylseleno)-1-bromoethylene (4). Chromatography gave pure E and Z forms (E/Z, 88/12): IR 1068 (m), 1020 (F), 1000 (m) cm^{-1}; NMR δ [E isomer] 7.10 (A, 1 H, CHBr), 6.39 (B, 1 H, $CHSeC_6H_5$) (J_{AB} = 13.7 Hz), [Z isomer] 6.64 (d, J = 6.25 Hz, 1 H). Anal. Calcd for C_8H_7BrSe: C, 36.67; H, 2.69, Found: C, 36.77; H, 2.68.

1,2-Bis(phenylseleno)ethylene (5). Chromatography gave pure E and Z forms as yellow to reddish oils (E/Z, 58/42): IR [E isomer] 1068 (m), 1020 (m), 1000 (m), 921 (m) [Z isomer] 1071 (m), 1022 (F), 1000 (m) cm^{-1}; NMR δ 7.73–7.13 (m, 10 H, C_6H_5), [E isomer] 6.91 (s, 2 H, CH=CH). [Z isomer] 7.18 (s, 2 H, CH=CH). Anal. Calcd for $C_{14}H_{16}Se_2$: C, 49.72; H, 3.58. Found: C, 49.58; H, 3.52.

β,β-Bis(phenylseleno)styrene (6): pale yellow solid, mp 66.4 °C; IR 1068 (m), 1021 (m), 1000 (F) cm^{-1}. NMR δ 7.70–7.03 (m). Anal. Calcd for $C_{20}H_{16}Se_2$: C, 58.00; H, 3.89. Found: C, 57.96; H, 3.78.

[1,1-Bis(phenylseleno)methylene]cyclohexane (7): yellow oil; IR 1069 (m), 1023 (F), 1001 (m) cm^{-1}; NMR δ 7.58–6.99 (m, 10 H, C_6H_5), 2.97–2.40 (m, 4 H) 1.87–1.35 (m, 6 H). Anal. Calcd for $C_{19}H_{20}Se_2$: C, 56.17; H, 4.94. Found: C, 56.10; H, 5.21.

1,1-Bis(phenylseleno)-1-nonene (8): red oil; IR 1066 (m), 1022 (F), 1000 (m) cm^{-1}; NMR δ 7.78–6.97 (m, 10 H, C_6H_5), 6.42 (t, 1 H, ^3J = 7 Hz, HC=), 2.65–1.98 (m, 2 H, CH_2CH=), 1.77–1.06 (m, 10 H $(CH_2)_5$), 1.06–0.63 (m, 3 H, CH_3). Anal. Calcd for $C_{21}H_{26}Se_2$: C, 57.80; H, 6.01. Found: C, 57.64; H, 6.20.

1,1-Bis(phenylseleno)-4-phenylbutadiene (9): pale yellow solid, mp 55 °C; IR 1062 (m), 1022 (m), 998 (m) cm^{-1}; NMR δ 7.77–7.1 (m, 16 H), 6.92 (part of AB system, J = 10.25 Hz, 1 H), 6.50 (part of AB system, J = 15 Hz, 1 H). Anal. Calcd for $C_{22}H_{18}Se_2$: C, 60.01; H, 4.12. Found: C, 59.95; H, 4.30.

Synthesis of Vinyl Sulfides and Ketene Thioacetals. The reactions were conducted in either dimethoxyethane or toluene using sodium phenyl thiolate. The reactions conditions and amounts of catalyst and reagents are mentioned in Table III. Those reactions that needed a temperature of 120 °C were conducted in sealed tubes. Treatments of reaction mixtures were identical with those for selenides.

2-(Phenylthio)-2-butene (10): colorless oil; IR 1001 (w), 1026 (s), 1070 (m) cm^{-1}; NMR δ 7.65–7.05 (m, 5 H, C_6H_5), 6.25–5.60 (m, 1 H, HC=), 2.12–1.63 (m, 6 H, CH_3). Anal. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.36. Found: C, 73.13; H, 7.34.

1-(Phenylthio)propene (11): colorless oil; IR 1003 (w), 1025 (s), 1065 (m) cm^{-1}; NMR δ 7.60–7.10 (m, 5 H, C_6H_5), 6.43–5.60 (m, 2 H, CH=CH), 1.80 (d, J = 6 Hz, 3 H, CH_3).

β-(Phenylthio)styrene (12): colorless oil; IR (1002 (w), 1026 (s), 1071 (m) cm^{-1}; NMR δ 7.67–7.02 (m, 10 H, C_6H_5), [AB system] 6.85 (A, 1 H, C_6H_5CH=), 6.71 (B, 1 H, C_6H_5SCH=) (J_{AB} = 15.5 Hz) [data compatible with the literature[13a]].

1-(Phenylthio)-2-(phenylseleno)ethylene (13): yellow oil (E/Z, 50:50). IR 1002 (w), 1025 (s), 1071 (m) cm^{-1}; NMR δ [E isomer] 6.82 (s, 2 H, CH=CH), [Z isomer, AB system] 6.79 (A), 6.63 (B) (J_{AB} = 11 Hz). Anal. Calcd for $C_{14}H_{22}SSe$: C, 57.73; H, 4.15. Found: C, 57.49; H, 4.17.

1,2-Bis(phenylthio)ethylene (14): yellow oil (E/Z, 80/20); IR and NMR spectra compared with those of an authentic sample; NMR δ 7.62–7.02 (m), [E isomer] 6.55 (s, 2 H, CH=CH).

β,β-Bis(phenylthio)styrene (15): white solid, mp 57 °C; IR 1002 (w), 1025 (s), 1074 (m); NMR δ 7.83–7.47 (m, 2 H), 7.47–7.15 (m, 14 H). Anal. Calcd for $C_{20}H_{16}S_2$: C, 74.96; H, 5.03. Found: C, 74.76; H, 5.23.

[1,1-Bis(phenylthio)methylene]cyclohexane (16): colorless viscous oil; IR 1001 (w), 1028 (s), 1071 (m) cm^{-1}; NMR δ 7.21 (s, 10 H, C_6H_5), 3.1–2.53 (m, 4 H), 1.97–1.40 (m, 6 H). Anal. Calcd for $C_{19}H_{20}S_2$: C, 73.03; H, 6.45. Found: C, 73.06; H, 6.43.

1,1-Bis(phenylthio)-1-nonene (17): colorless viscous oil; IR 1000 (w), 1027 (s), 1070 (m); NMR δ 7.67–7.15 (m, 10 H, C_6H_5), 6.4 (t, J = 7 Hz, 1 H), 2.88–2.1 (m, 2 H), 1.97–1.15 (m, 10 H, CH_2), 1.15–0.63 (m, 3 H, CH_3).

1,1-Bis(phenylthio)-4-phenylbutadiene (18): brown viscous oil; IR 1001 (w), 1026 (s), 1070 (m), cm^{-1}; NMR δ 7.72–6.98 (m, 16 H, C_6H_5 and $C_6H_5C{=}CH$), 6.85 (part of AB system, (1 H, J = 10.5 Hz, $(C_6H_5S)_2C{=}CH$), 6.58 (part of AB system, (1 H, J = 16 Hz, $C_6H_5C{=}CH$). Anal. Calcd for $C_{22}H_{18}S_2$: C, 72.25; H, 5.23. Found: C, 72.25; H, 5.14.

Registry No. (*E*)-**1**, 24225-10-3; (*Z*)-**1**, 24213-07-8; (*E*)-**2**, 68001-61-6; (*Z*)-**2**, 68001-62-7; (*E*)-**3**, 60466-40-2; (*Z*)-**3**, 60466-30-0; (*E*)-**4**, 26620-10-0; (*Z*)-**4**, 100230-65-7; (*E*)-**5**, 95391-88-1; (*Z*)-**5**, 7392-11-2; **6**, 62762-11-2; **7**, 89438-16-4; **8**, 100230-66-8; **9**, 100230-67-9; **10**, 16336-52-0; **11**, 22103-05-5; **12**, 16619-61-7; (*E*)-**14**, 18893-63-5; (*Z*)-**14**, 18893-62-4; **15**, 35550-81-3; **16**, 69190-57-4; **17**, 100230-68-0; **18**, 100230-69-1; (*E*)-**13**, 95391-85-8; (*Z*)-**13**, 7392-12-3; $(bipy)_2NiBr_2$, 15555-11-0; C_6H_5SeNa, 23974-72-3; C_6H_5SNa, 930-69-8; 1,1-dibromo-4-phenylbutadiene, 90766-67-9; 1,1-dibromo-2-phenylethylene, 7436-90-0; 1,1-dibromo-1-octene, 73383-25-2; (*E*)-2-bromo-2-butene, 3017-71-8; 1-bromopropene, 590-14-7; (*E*)-styryl bromide, 588-72-7; 1,2-dibromoethane, 106-93-4; (dibromomethylene)cyclohexane, 60014-85-9; (*Z*)-styryl bromide, 588-73-8; (*Z*)-2-bromo-2-butene, 3017-68-3.

(18) Posner, G. H.; Loomis, G. L.; Sawaya, H. S. *Tetrahedron Lett.* **1975**, *16*, 1373.

(19) Sharpless, K. B.; Lauser, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.