

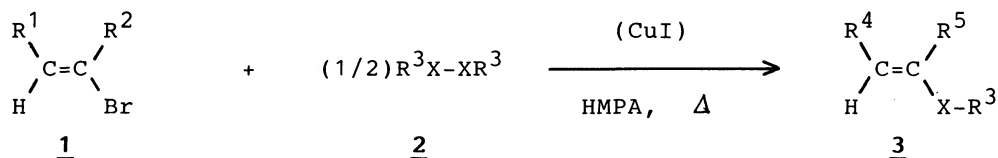
A Direct Formation of Alkenyl Chalcogenides from Nonactivated Alkenyl  
Halides and Diorganyl Dichalcogenides under Neutral Conditions

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Alkenyl sulfides and selenides were easily obtained in moderate to good yields by heating the corresponding bromides with diorganyl disulfides or diselenides in hexamethylphosphoric triamide with or without copper(I) iodide as a promoter.

Alkenyl chalcogenides undergo a variety of functional group transformations valuable for organic synthesis. Although these compounds can be obtained from the reaction of alkenyl halides with chalcogenide anion, this procedure usually requires long reaction time and/or strongly basic conditions, where the yields are often low and products separation is quite laborious due to concurrent side reactions. Thus almost all of such procedures currently in use involve the replacement of a halogen atom by a chalcogenide anion under the assistance of transition metal catalysts.<sup>1)</sup>

The purpose of this paper is to describe a new type of nucleophilic substitution reaction of alkenyl halides with diorganyl dichalcogenides, where neither the generation of anionic species nor the use of transition metal catalyst is required; simple heating of dichalcogenide (2) with alkenyl bromide (1) in



|          | R <sup>1</sup>                                  | R <sup>2</sup>                                | R <sup>3</sup>                                  | R <sup>4</sup>                                  | R <sup>5</sup>  | X  |
|----------|---|---|---|---|-----------------|----|
| <u>a</u> | C <sub>6</sub> H <sub>5</sub>                   | H   | C <sub>6</sub> H <sub>5</sub>                   | C <sub>6</sub> H <sub>5</sub>                   | H               | S  |
| <u>b</u> | C <sub>6</sub> H <sub>5</sub>                   | H   | C <sub>6</sub> H <sub>5</sub>                   | C <sub>6</sub> H <sub>5</sub>                   | H               | Se |
| <u>c</u> | C <sub>6</sub> H <sub>5</sub>                   | H   | 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> | C <sub>6</sub> H <sub>5</sub>                   | H               | S  |
| <u>d</u> | C <sub>6</sub> H <sub>5</sub>                   | H   | (CH <sub>3</sub> ) <sub>3</sub> C               | C <sub>6</sub> H <sub>5</sub>                   | H               | S  |
| <u>e</u> | H   | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> | C <sub>6</sub> H <sub>5</sub>                   | C <sub>6</sub> H <sub>5</sub>                   | CH <sub>3</sub> | S  |
| <u>f</u> | H   | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> | C <sub>6</sub> H <sub>5</sub>                   | C <sub>6</sub> H <sub>5</sub>                   | CH <sub>3</sub> | Se |
| <u>g</u> | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> | H   | C <sub>6</sub> H <sub>5</sub>                   | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> | H               | S  |

Table 1. Preparation of alkenyl chalcogenides from alkenyl halides and diorganyl dichalcogenides in the presence of copper(I) iodides<sup>a)</sup>

| Entry | Alkenyl   | Diorganyl      | Cu(I) | Time | Alkenyl chalcogenide <u>3</u> |                     |                    |
|-------|-----------|----------------|-------|------|-------------------------------|---------------------|--------------------|
|       | bromide   | dichalcogenide |       |      | Conv. <sup>b)</sup>           | Yield <sup>c)</sup> |                    |
|       | <u>1</u>  | <u>2</u>       | mmol  | h    | %                             | %                   |                    |
| 1     | <u>1a</u> | <u>2a</u>      | 2     | 2    | <u>3a</u>                     | 97                  | 87 <sup>d)</sup>   |
| 2     | <u>1a</u> | <u>2a</u>      | 0     | 12   | <u>3a</u>                     | 68                  | 82 <sup>d)</sup>   |
| 3     | <u>1a</u> | <u>2b</u>      | 2     | 7    | <u>3b</u>                     | 96                  | 56 <sup>d)</sup>   |
| 4     | <u>1a</u> | <u>2b</u>      | 0     | 5    | <u>3b</u>                     | 98                  | 97 <sup>d)</sup>   |
| 5     | <u>1a</u> | <u>2c</u>      | 2     | 7    | <u>3c</u>                     | 99                  | 48 <sup>e)</sup>   |
| 6     | <u>1a</u> | <u>2c</u>      | 0     | 11   | --                            | 80                  | 0 <sup>f)</sup>    |
| 7     | <u>1a</u> | <u>2d</u>      | 2     | 24   | <u>3d</u>                     | 93                  | 45 <sup>e,g)</sup> |
| 8     | <u>1a</u> | <u>2d</u>      | 0     | 6    | --                            | 0                   | 0                  |
| 9     | <u>1e</u> | <u>2e</u>      | 2     | 6    | <u>3e</u>                     | 92                  | 60 <sup>h)</sup>   |
| 10    | <u>1e</u> | <u>2e</u>      | 0     | 11   | <u>3e</u>                     | 97                  | 58 <sup>h)</sup>   |
| 11    | <u>1e</u> | <u>2f</u>      | 2     | 4    | <u>3f</u>                     | 91                  | 68 <sup>h)</sup>   |
| 12    | <u>1e</u> | <u>2f</u>      | 0     | 10   | --                            | 55                  | 0 <sup>i)</sup>    |
| 13    | <u>1g</u> | <u>2g</u>      | 2     | 10   | <u>3g</u>                     | 100                 | 75                 |

a) Alkenyl halide, 2 mmol; dichalcogenide, 1 mmol; HMPA, 2 ml. b) Conversions based on dichalcogenide. c) Yields based on unrecovered dichalcogenide refer to the isolated pure product and are not optimized. d) E/Z = ca. 5/1. e) E/Z > 99/1. f) Only polymeric product was obtained. g) Bis(2-phenylethenyl) sulfide was obtained as by-product in 23% yield. h) An E/Z isomeric mixture of 1-methyl-2-phenylethenyl phenyl sulfide or selenide was the respective product. The isomeric ratios were variable. i) A complex reaction mixture was obtained.

hexamethylphosphoric triamide (HMPA) in the presence or absence of copper(I) iodide affords the corresponding alkenyl chalcogenide (3) in moderate to good yields.<sup>2-4)</sup> The starting materials are easily available and the manipulation is extremely simple.

A typical procedure is as follows; a mixture of 1-bromo-2-phenylethene (2 mmol, 366 mg), diphenyl disulfide (1 mmol, 218 mg), copper(I) iodide (2 mmol, 380 mg) and hexamethylphosphoric triamide (HMPA) (2 ml) was heated for 2 h at 160 °C under nitrogen. Usual workup followed by chromatographic purification on silica gel gave 358 mg (87 %) of phenyl 2-phenylethenyl sulfide (3a) (Table 1, entry 1).

The substitution reaction readily occurred not only with conjugated alkenyl bromide (2-bromo-1-phenylethene, entries 1-8) but also with non-conjugated alkenyl bromide (1-bromo-1-octene and 2-bromo-1-phenyl-2-propene entries 9-13). The latter bromide underwent the sulfenylation with simultaneous isomerization to afford phenyl 1-phenyl-2-propenyl sulfide (**3e**). Reactions with aliphatic disulfide led to the corresponding alkenyl sulfide in an acceptable yield (entry 7).

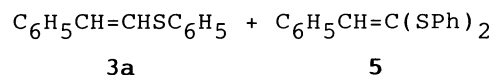
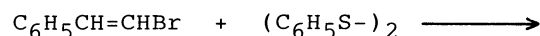
With diselenide the replacement of a halogen atom proceeded smoothly even in the absence of copper(I) iodide (Table 1, entry 4). This result is noteworthy because the direct substitution of a halogen on a vinylic position by a selenolate anion has only one precedence in the literature.<sup>1)</sup> With less nucleophilic dichalcogenides such as diphenyl disulfide and bis(4-nitrophenyl) disulfide, more drastic conditions were required to perform the reactions without copper(I) iodide. For the reactions with aliphatic disulfide, the use of catalyst was indispensable and no reaction was observed in the absence of copper(I) iodide. Of many copper salts examined (CuI, CuBr, CuCl, CuSCN, CuCN, CuSO<sub>4</sub>, Cu(OAc)<sub>2</sub>, and CuCl<sub>2</sub>), copper(I) iodide was the only compound that could promote the sulfenylation efficiently.

The reactions of 1-bromo-2-phenylethene with diphenyl disulfide were compared in several solvent systems; in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) sulfide **3a** was obtained together with appreciable amounts of disubstituted product (**5**). In dimethylaniline (DMA), tetrahydrofuran (THF) and 1,4-dioxane, no sulfides were produced (Table 2).

We expect that the present procedure will constitute a simple and economical alternative to alkenyl sulfides and selenides. Furthermore, the reaction is of mechanistic interest in view of the ease with which nucleophilic vinylic substitution reaction takes place under completely neutral conditions.

#### References

Table 2. Sulfide formation in various solvents<sup>a)</sup>



| Solvent | Temp<br>°C | Conv<br>% | Yield/%   |          |
|---------|------------|-----------|-----------|----------|
|         |            |           | <b>3a</b> | <b>5</b> |
| HMPA    | 160        | 97        | 87        | 1        |
| DMF     | 160        | 52        | 44        | 14       |
| DMSO    | 160        | 66        | 36        | 48       |
| DMA     | 160        | 63        | 0         | 0        |
| THF     | 67         | 20        | 0         | 0        |
| Dioxane | 101        | 47        | 0         | 0        |

a) Alkenyl bromide, 2 mmol; dichalcogenide, 1 mmol; copper(I) iodide 2 mmol; solvent, 2 ml; 2 h.

- 1) For recent examples, see H. J. Cristau, B. Chabaud, R. Labaudiniere, and H. Christol, *J. Org. Chem.*, **51**, 875 (1986); M. Foa, R. Santi, and F. Cavaglia, *J. Organomet. Chem.*, **206**, C29 (1981); S. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kondo, *J. Org. Chem.*, **44**, 2408 (1979).
- 2) Activation by HMPA of vinylic substitution has recently been reported; M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, and M. Montanucci, *J. Org. Chem.*, **48**, 4795 (1983);
- 3) As for the CuI activated substitution of alkenyl halides in HMPA, see; H. Suzuki, M. Aihara, H. Yamamoto, Y. Takamoto, and T. Ogawa, *Synthesis*, **1988**, 236; T. Ogawa, K. Kusume, M. Tanaka, and H. Suzuki, *Synth. Commun.*, in the press.
- 4) Spectral and analytical data of some representative products are as follows;  
**Phenyl 2-phenylethenyl sulfide (3a)**: bp 150-160 °C / 7 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 6.45 (d,  $J=11$  Hz, 1H, vinyl proton of cis isomer), 6.57 (d,  $J=11$  Hz, 1H, vinyl proton of cis isomer), 6.73 (d,  $J=16$  Hz, 1H, vinyl proton of trans isomer), 6.87 (d,  $J=16$  Hz, 1H, vinyl proton of trans isomer), 7.2 - 7.5 (m, 10H); IR (NaCl) 1575, 1470, 1435, 940, 735, and 680  $\text{cm}^{-1}$ ; MS (rel. intensity) 212 ( $\text{M}^+$ , 100), 167 (20), 135 (12), 121 (26), and 103 (7). Found: C, 78.89; H, 5.74%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{S}$ : C, 79.20; H, 5.70%.  
**Phenyl 2-phenylethenyl selenide (3b)**: bp 169-175 °C / 9 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 6.77 (d,  $J=10$  Hz, 1H, vinyl proton of cis isomer), 6.86 (d,  $J=16$  Hz, vinyl proton of trans isomer), 6.96 (d,  $J=10$  Hz, 1H, vinyl proton of cis isomer), 7.16 (d,  $J=16$  Hz, 1H, vinyl proton of trans isomer), 7.26-7.32 (m, 5H), 7.51-7.55 (m, 5H); IR (NaCl) 1595, 1570, 1470, 1435, 1020, 940, 730, and 680  $\text{cm}^{-1}$ ; MS (rel. intensity) 260 ( $\text{M}^+$ , 100), 180 (96), and 169 (58). Found: C, 65.05; H, 4.84%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{Se}$ : C, 64.87; H, 4.67%.  
**4-Nitrophenyl 2-phenylethenyl sulfide (3c)**: pale yellow crystals, mp 111-113 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 6.87 (d,  $J=15$  Hz, 1H), 7.02 (d,  $J=15$  Hz, 1H), 7.32-7.52 (m, 5H), 8.13-8.18 (m, 4H); IR (KBr) 1575, 1495, 1340, 1085, 955, 850, 840, 740, and 685  $\text{cm}^{-1}$ ; MS (rel. intensity) 257 ( $\text{M}^+$ , 100), 210 (16), 178 (22), and 135 (10). Found: C, 65.05; H, 4.20; N, 5.45%. Calcd for  $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{S}$ : C, 65.35; H, 4.31; N, 5.44%.  
**1,1-Dimethylethyl 2-phenylethyl sulfide (3d)**: bp 70-79 °C / 3 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 1.38 (s, 9H), 6.69 (d,  $J=15$  Hz, 1H), 6.72 (d,  $J=15$  Hz, 1H) and 7.21 (bm, 5H); IR (NaCl) 2950, 1590, 1360, 1160, 940, 735, and 685  $\text{cm}^{-1}$ ; MS (rel. intensity) 192 (61), 136 (100), 91 (28), and 57 (62). Found: C, 75.03; H, 8.25%. Calcd for  $\text{C}_{12}\text{H}_{16}\text{S}$ : C, 74.94; H, 8.39%.  
**1-Methyl-2-phenylethenyl phenyl sulfide (3e)**: bp 120-124 °C / 2.5 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 2.03 (d,  $J=1$  Hz, 3H, methyl proton of one isomer), 2.13 (d,  $J=1$  Hz, 3H, methyl proton of another isomer), 6.68 (bs, 1H, vinyl proton of one isomer), 6.71 (bs, 1H, vinyl proton of another isomer), 7.19-7.56 (m, 10H); IR (NaCl) 1575, 1465, 1435, 1020, 780, 740, and 680  $\text{cm}^{-1}$ ; MS (rel. intensity) 226 ( $\text{M}^+$ , 63), 149 (100), and 117 (22). Found: C, 79.63; H, 6.29%. Calcd for  $\text{C}_{15}\text{H}_{14}\text{S}$ : C, 79.60; H, 6.23%.  
**1-Phenyl-2,2-bis(phenylthio)ethene (5)**: bp 175-180 °C / 2.5 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 6.86 (s, 1H) and 7.02-7.56 (m, 15H); MS (rel. intensity) 320 ( $\text{M}^+$ , 36), 212 (100), 167 (28), 135 (14), and 121 (25). Found: C, 74.90; H, 5.13%. Calcd for  $\text{C}_{20}\text{H}_{16}\text{S}_2$ : C, 74.95; H, 5.27%.  
**1-Octenyl phenyl sulfide (3g)**: colorless oil, bp 120-125 °C / 1 Torr.

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