Tetrahedron Vol. 42, No. 16, pp. 4577 to 4584, 1986
Printed in Great Britain.

0040–4020/86 $3.00+.00

STEREOSPECIFIC SYNTHESIS OF DIVINYL DISELENIDES FROM VINYL ACETYL SELENIDES

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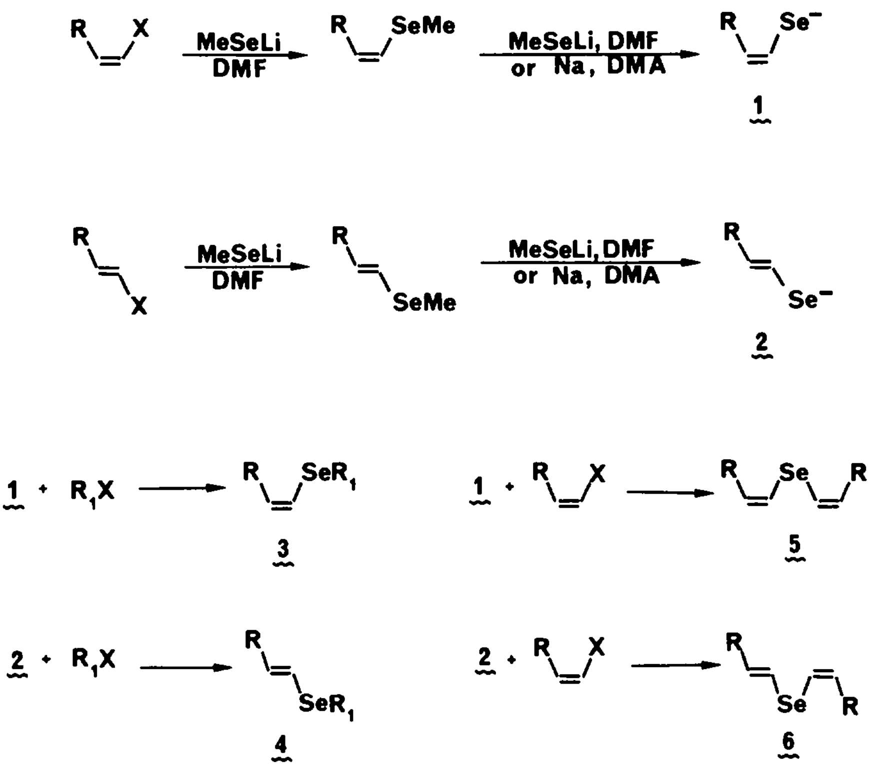
(*Received in UK* 12 *May* 1986)

Abstract. Vinyl halides react with MeSeLi in DMF to afford vinyl methyl selenides which are demethylated by the excess of the MeSeLi; the vinyl selenide anions thus obtained react with acetyl chloride to give vinyl acetyl selenides. This three steps one pot synthesis occurs with complete retention of configuration. The vinyl acetyl selenides are cleanly fragmented by electron transfer to the vinyl selenide anions; addition of iodine to the resulting solutions produced the divinyl diselenides with retention of configuration. The transformation of vinyl acetyl selenides into divinyl diselenides can also be induced by catalytic amounts of a solution of sodium in HMPA or of sodium methanethiolate.

We have recently reported that unactivated vinyl halides react with selenium nucleophiles in DMF to give the products of vinylic substitution with complete retention of configuration.[1] Thus vinyl halides react with lithium methyl selenide to afford vinyl methyl selenides (Scheme 1). Under more severe conditions and with an excess of MeSeLi the reaction products suffer a nucleophilic aliphatic substitution and are demethylated to the vinyl selenide anions (1) and (2).[2,3] Under the conditions employed these anions retain the configuration of the starting products (Scheme 1) and do not interconvert. The same results are obtained if the demethylation reaction is effected with sodium in DMA.[4] The anions (1) and (2) react with several alkyl halides to give a series of vinyl alkyl selenides (3) and (4).[2] The same anions also react with unactivated vinyl halides to give symmetrical and unsymmetrical divinyl selenides (5) and (6). Also in this case the substitution reaction occurred with retention of configuration (Scheme 1).[4]

SCHEME 1



R = Ph, PhS, PhSe $\qquad$ R_1 = Et-, Me_2CH-, CH_2=CH-CH_2-

We now report that the anions (1) and (2) react cleanly with acyl chlorides to afford the corresponding vinyl acyl selenides in good yields. The fragmentation of these compounds represents the cleanest way for the stereospecific preparation of the vinyl selenide anions (1) and (2). The oxidation of these anions with iodine affords the corresponding divinyl diselenides in good yields and in a stereospecific way. Thus divinyl diselenides are produced from vinyl halides according to the various steps which are indicated in the following reactions for a generic vinylic substrate:

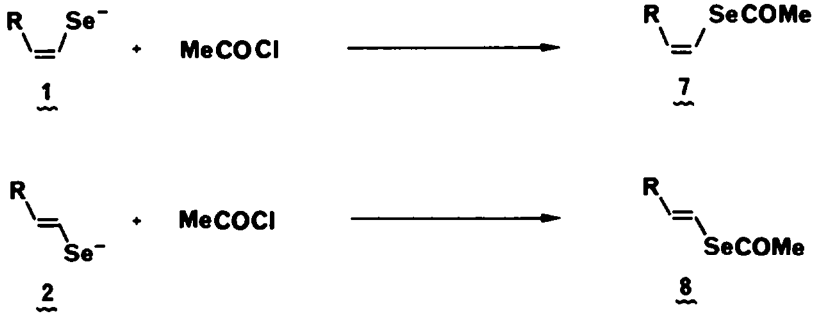
$$\mathrm{VinX} \longrightarrow \mathrm{VinSeMe} \longrightarrow \mathrm{VinSe}^- \longrightarrow \mathrm{VinSeCOMe} \longrightarrow \mathrm{VinSeSeVin}$$

The first three steps can be effected in one pot and the present procedure represents therefore a convenient way to effect the stereospecific synthesis of symmetrical divinyl diselenides.

RESULTS AND DISCUSSION

Vinyl halides react with excess MeSeLi, at 100°C in DMF under nitrogen, to give the vinyl selenide anions (1) and (2) (See Scheme 1); addition of acetyl chloride to the cooled solutions, followed by the usual work up and column chromatography, afforded the vinyl acetyl selenides (7a–c) and (8a–c) in yields ranging from 65 to 90% (Scheme 2).

SCHEME 2

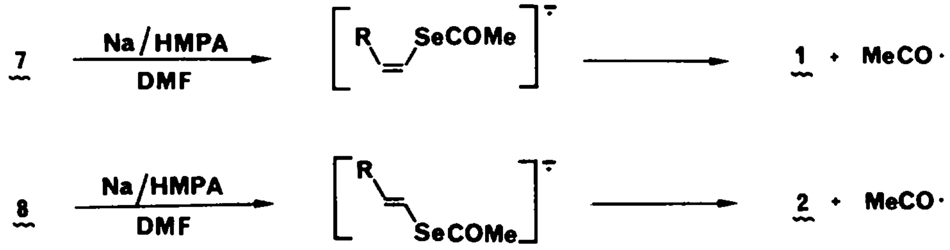


a : R = Ph ; b : R = PhS ; c : R = PhSe

The anion (2a) was also treated with benzoyl chloride and the (E)-β-styryl benzoyl selenide, PhCH=CHSeCOPh, was isolated in 70% yields. This reaction therefore seems to be a general one and other acyl halides can very likely give similar good results. Since excess MeSeLi is used for the production of (1) and (2), MeSeCOMe and MeSeCOPh are also formed as by-products in these reactions; both these compounds however are easily eliminated during the work up or the column chromatography of the reaction mixtures.

Vinyl acetyl selenides are very easily fragmented by electron transfer to give back the vinyl selenide anions. Thus, when a solution of (7) or (8) in DMF is treated, under nitrogen at room temperature, with an equimolecular amount of a solution of sodium in HMPA, (1) and (2) were obtained in quantitative yields, as demonstrated by the isolation of the (Z)- and (E)-β-(methylselenyl)styrene, respectively, after addition of methyl iodide. Very likely these reactions proceed through the intermediate formation of the corresponding radical anions which suffer a fast fragmentation into (1) and (2) and acetyl radicals (Scheme 3).

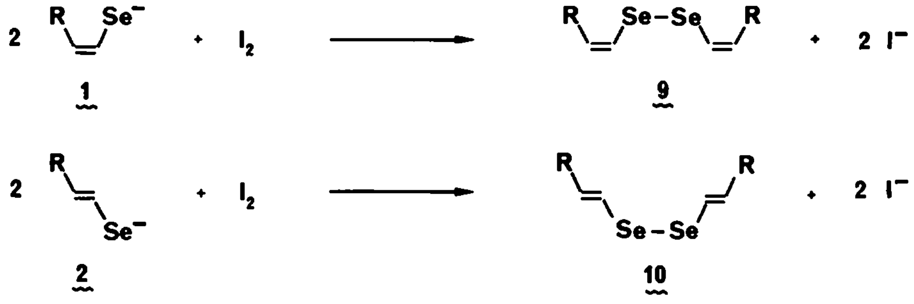
SCHEME 3



The fate of the proposed acetyl radicals was beyond the scope of the present work and was therefore not investigated. A similar fragmentation reaction was also observed in the case of the corresponding vinyl alkyl selenides;[4] in that case however more severe experimental conditions were required (100°C; 3 - 6 h). Moreover, when the reaction was applied to the (Z)- and (E)-1-phenylselenyl-2-methylselenyl ethylenes the fragmentation occurred at the arylselenium vinyl bond to afford the phenyl selenide anion. In the present case, on the contrary, the corresponding acetates afforded cleanly the desired anions (1c) and (2c). Clearly the vinyl acetyl selenides have a greater electron affinity than the corresponding vinyl alkyl selenides and their radical anions are also more easily fragmented; the fragmentation involves in every case the selenium acetyl bond. The procedure now described to produce the vinyl selenide anions (1) and (2) is very mild and offers several advantages over those reported in the previous paper and consisting in the dealkylation of vinyl alkyl selenides by means of MeSeLi[2,3] or of sodium[4] (See Scheme 1). We have already applied the present method for the stereospecific synthesis of divinyl selenides with very satisfactory results.[4] A very clean method of production of (1) and (2) is an essential prerequisite for the successful synthesis of the divinyl diselenides which is described below.

Oxidation of (1) and (2) afforded the divinyl diselenides (9) and (10) in good yields with complete retention of configuration. Although this conversion can be effected by air, as it is reported for the synthesis of diaryl diselenides from aryl selenide anions,[5] we have found that better results can be obtained if the oxidation is carried out with iodine.[6] Thus, the DMF solutions of (1) and (2), prepared as described above, were diluted with 10% sodium carbonate and iodine was added in small portions. The divinyl diselenides (9) and (10) separated from the solution as orange oils (Scheme 4).

SCHEME 4



a: R = Ph; b: R = PhS; c: R = PhSe

After the usual work up most of the diselenides were obtained in pure form and no further purification was needed. This was very important since these compounds were not very stable and easily decomposed on warming or on attempted column chromatography on silica gel or in alumina.[7] The only way in which we succeeded in the purification of some divinyl diselenides was to wash the solid or oily residue with cold light petroleum; better results were obtained by using cold ethanol but in this case a substantial loss of product occurred. Several difficulties were encountered in the preparation of the compounds containing four selenium atoms in the molecule, i.e. compounds (9c) and (10c), and analytically pure samples could not be obtained; nevertheless spectral data of the available compounds were in agreement with the proposed structures.

Although other possible mechanisms for the transformation of (1) into (9) and of (2) into (10) can be envisaged, a likely assumption is that (1) and (2) are first oxidized to the corresponding radicals which then dimerize. If this interpretation is correct, one has to assume that the vinyl selenyl radicals, like the corresponding anions, retain their configuration and do not interconvert; in fact, under the experimental conditions employed in the present work, the divinyl diselenides are formed with retention of configuration.[8]

The (E)- and (Z)-β-styryl acetyl selenides, (7a) and (8a), under the influence of catalytic amounts of sodium or of sodium methanethiolate, in DMF at room temperature under nitrogen, were transformed into the corresponding (E)- and (Z)-β-styryl diselenides, (9a) and (10a), in good yields. Similarly, (10a) was also obtained from the decomposition of the (E)-β-styryl benzoyl selenide induced by catalytic amounts of the solution of sodium in HMPA. Independent experiments showed that the styryl acetyl selenides, when dissolved in DMF, do not suffer any decomposition; they were in fact recovered unchanged after 24 h at 40°C. The observed transformation into the diselenides thus does not occur thermally but it requires sodium or methanethiolate anions to be stimulated. Since both these reagents are good electron donors and the vinyl acetyl selenides are good electron acceptors it could be suggested that an electron transfer occurs to afford the radical anions of the vinyl acetyl selenides. This could be the first step of a chain mechanism, involving vinyl acetyl selenide radical anions and vinyl selenide anions, from which vinyl selenyl radicals are produced; these radicals then dimerize to the divinyl diselenides. The various steps of the proposed mechanism are indicated below for a generic vinyl acetyl selenide:[9]

$$\mathrm{VinSeCOMe} \xrightarrow{e} \left[\mathrm{VinSeCOMe}\right]^{\dot{-}}$$

$$\left[\mathrm{VinSeCOMe}\right]^{\dot{-}} \longrightarrow \mathrm{VinSe}^{-} + \mathrm{MeCO}\cdot$$

$$\mathrm{VinSe}^{-} + \mathrm{VinSeCOMe} \longrightarrow \left[\mathrm{VinSeCOMe}\right]^{\dot{-}} + \mathrm{VinSe}\cdot$$

$$2\ \mathrm{VinSe}\cdot \longrightarrow \mathrm{VinSeSeVin}$$

Since the divinyl diselenides are produced with retention of configuration, if this mechanism is correct, once again one has to assume that vinyl selenyl radicals do not interconvert under the experimental conditions employed. This decomposition reaction seems not to be limited to vinylic substrates. Under the same conditions (catalytic amounts of sodium in HMPA or of MeSNa), the phenyl acetyl selenide, PhSeCOMe, was converted into diphenyl diselenide in good yields. Further work is necessary and is presently under way to find other experimental evidences for the mechanism proposed above.

The results presented in this paper show that vinyl acyl selenides can be very easily obtained and are very versatile selenium derivatives which can find synthetic applications other than those described by us in the present and in the previous paper.[4] To our knowledge the divinyl diselenides described in this work represent the first examples of this kind of compounds; previous synthesis of diselenides were in fact mainly concerned with symmetrical diaryl[5,6,10] or dialkyl[11] or unsymmetrical alkyl methyl and alkyl phenyl derivatives.[12]

EXPERIMENTAL

The structures of the vinyl acetyl selenides (**7**) and (**8**) and of the divinyl diselenides (**9**) and (**10**) were assigned on the basis of their proton, carbon-13 and mass spectra, and of their elemental analyses. Proton nmr spectra were recorded at 90 MHz on a Varian EM 390 instrument in $CDCl_3$ solutions and, in some cases, in C_6D_6 (TMS as reference). Carbon-13 nmr spectra were recorded ($CDCl_3$ solutions, TMS as reference) at 20.15 MHz on a Bruker WP 80 SY instrument operating in the Fourier transform mode with proton decoupling throughout. Mass spectra were obtained with a Varian MAT 311 A instrument at 35 eV using an all glass inlet system. The presence of six natural isotopes of selenium leads to highly characteristic groups of picks for selenium containing fragments, but at the same time makes the analysis of these picks more difficult.[12,13] The values reported below refer only to the prominent picks; for the ions containing selenium only the pick arising from the ^{80}Se isotope is given. Elemental analyses were carried out on a Carlo Erba Model 1106 Elemental Analyzer. Glc analyses were performed on a Hewlett-Packard 5830 A chromatograph with a 20 in., 10% UCW 982 column.

(Z)- and (E)-β-Bromostyrenes, (Z)- and (E)-1-chloro-2-phenylthioethylene, (Z)- and (E)-1-chloro-2-phenylselenylethylene were prepared as described in previous works.[1,4]

Synthesis of the Vinyl Acetyl Selenides, (7) and (8).

To a solution of lithium methyl selenide (20 mmol) in THF, prepared as described in previous works,[14,15] a solution of the vinyl halide (5 mmol) in DMF (15 ml) was added. The flask was immersed into a silicon oil bath kept at 100°C and the THF was left to distill off under nitrogen. The mixture was stirred at this temperature until the starting product was consumed and the vinyl methyl selenide was dealkylated to the corresponding vinyl selenide anion (2 - 3 h). The progress of the reaction was monitored by glc after treatment of small aliquots of the reaction mixture with ethyl iodide. The reaction mixture was cooled in an ice bath and excess acetyl chloride (or benzoyl chloride) (30 mmol) was added dropwise. The resulting colourless solution was poured on 10% sodium carbonate solution and extracted with ether. The ether was washed with water, dried and evaporated. The reaction product was isolated and purified by column chromatography on silica gel using a mixture of light petroleum and ether (98 : 2) as eluant. The reaction yields and the physical and spectral data of the products obtained are reported below.

(Z)-β-Styryl acetyl selenide, (**7a**), (80%), m.p. 54-5°C. ^1H-nmr δ 7.3 (m, 5H), 7.0 (s, 2H), 2.45 (s, 3H); in C_6D_6, δ 7.25 - 7.0 (m, 5H), 7.2 (d, 1H, J = 10.5 Hz), 6.8 (d, 1H, J = 10.5 Hz), 1.85 (s, 3H). ^{13}C-nmr δ 194.4 (CO), 137.3 (ipso-C), 131.2 (α-vin-C), 128.5 (o-C), 128.4 (m-C), 127.6 (p-C), 118.1 (β-vin-C), 34.7 (CH_3). Mass, m/e 225 (22), 183 (60), 102 (31), 43 (100). Anal. Calcd for $C_{10}H_{10}OSe$: C, 53.34; H, 4.49. Found: C, 53.70; H, 4.48.

(E)-β-Styryl acetyl selenide, (**8a**), (86%), m.p. 48-9°C. ^1H-nmr δ 7.25 - 7.1 (m, 5H), 7.15 (d, 1H, J = 16 Hz), 6.85 (d, 1H, J = 16 Hz), 2.35 (s, 3H). ^{13}C-nmr δ 195.5 (CO), 136.7 (ipso-C), 134.9 (α-vin-C), 128.6 (o-C), 127.9 (p-C), 126.3 (m-C), 116.6 (β-vin-C), 34.5 (CH_3). Mass, m/e 225 (15), 183 (56), 102 (33), 43 (100). Anal. Calcd for $C_{10}H_{10}OSe$: C, 53.34; H, 4.49. Found: C, 53.05; H, 4.44.

(E)-β-Styryl benzoyl selenide, (69%), m.p. 93-5°C. ^1H-nmr δ 7.95 - 7.8 (m, 2H), 7.6 - 7.2 (m, 8H), 7.55 (d, 1H, J = 16 Hz), 6.95 (d, 1H, J = 16 Hz). Mass, m/e 287 (5), 105 (100), 77 (8). Anal. Calcd for $C_{15}H_{12}OSe$: C, 62.72; H, 4.22. Found: C, 63.00; H, 4.18.

(Z)-2-Phenylthio-1-ethenyl acetyl selenide, (**7b**), (89%), m.p. 39-41°C. ^1H-nmr δ 7.4 - 7.2 (m, 5H), 7.0 (d, 1H, J = 10 Hz), 6.8 (d, 1H, J = 10 Hz), 2.45 (s, 3H). ^{13}C-nmr δ 193.9 (CO), 134.8 (ipso-C), 129.7 (o-C), 129.2 (m-C), 127.8 (α-vin-C), 127.1 (p-C), 119.8 (β-vin-C), 34.7 (CH_3). Mass, m/e 258 (94), 216 (100), 135 (7), 43 (10). Anal. Calcd for $C_{10}H_{10}OSSe$: C, 46.69; H, 3.93. Found: C, 46.90; H, 3.85.

(E)-2-Phenylthio-1-ethenyl acetyl selenide, (**8b**), (76%), m.p. 58-60°C. ^1H-nmr δ 7.3 - 7.15 (m, 5H), 6.7 (d, 1H, J = 15.5 Hz), 6.6 (d, 1H, J = 15.5 Hz), 2.4 (s, 3H). ^{13}C-nmr δ 195.4 (CO), 133.9 (ipso-C), 130.5 and 129.2 (o-, m-, p-C), 127.4 (α-vin-C), 115.3 (β-vin-C), 34.2 (CH_3). Mass, m/e 257 (48), 215 (100), 134 (35), 104 (22), 43 (79). Anal. Calcd for $C_{10}H_{10}OSSe$: C, 46.69; H, 3.93. Found: C, 46.95; H, 3.95.

(Z)-2-Phenylselenyl-1-ethenyl acetyl selenide, (**7c**), (68%), m.p. 23-4°C. ^1H-nmr δ 7.45 - 7.0 (m, 7H), 2.4 (s, 3H); in C_6D_6, δ 7.45 (d, 1H, J = 8.5 Hz), 7.35 - 7.1 (m, 2H), 7.0 - 6.95 (m, 3H), 6.9 (d, 1H, J = 8.5 Hz), 1.8 (s, 3H). ^{13}C-nmr δ 193.7 (CO), 132.1 (o-C), 130.2 (ipso-C), 129.3 (m-C), 127.4 (p-C), 125.3 (α-vin-C), 123.3 (β-vin-C), 34.6 (CH_3). Mass, m/e 306 (35), 264 (62), 182 (31), 104 (71), 103 (30), 43 (100). Anal. Calcd for $C_{10}H_{10}OSe_2$: C, 39.49; H, 3.32. Found: C, 39.8; H, 3.42.

(E)-2-Phenylselenyl-1-ethenyl acetyl selenide, (8c), (80%), m.p. 31-3°C. H-nmr δ 7.6 - 7.4 (m, 2H), 7.3 - 7.15 (m, 3H), 6.85 (s, 2H), 2.4 (s, 3H); in C_6D_6, δ 7.45 - 7.25 (m, 2H), 7.15 - 6.95 (m, 2H), 6.9 (d, 1H, J = 16 Hz), 6.7 (d, 1H, J = 16 Hz), 1.9 (s, 3H). ^{13}C-nmr δ 195.2 (CO), 132.9 (o-C), 129.3 (m-C), 129.2 (ipso-C), 127.7 (p-C), 124.5 (α-vin-C), 118.1 (β-vin-C), 34.2 (CH_3). Mass, m/e 306 (44), 264 (89), 182 (34), 104 (72), 103 (28), 43 (100). Anal. Calcd for $C_{10}H_{10}OSe_2$: C, 39.49; H, 3.32. Found: C, 40.02; H, 3.38.

Synthesis of the Divinyl Diselenides (9) and (10).

Sodium (0.25 g) was added to HMPA (10 ml), stirred under nitrogen at 100°C. The resulting solution was cooled at room temperature. This solution (1 ml) was added to a stirred solution of the vinyl acetyl selenide (1 mmol) in DMF (10 ml) kept under nitrogen at room temperature. After half an hour the starting product was completely fragmented (tlc). A 10% solution of sodium carbonate (15 ml) was added. To the resulting solution iodine was added in small portions until it was consumed. An orange viscous oil separated during the addition. The resulting mixture was diluted with water, saturated with sodium chloride, and extracted with ether. The ether was washed with a saturated solution of NaCl, dried and evaporated at room temperature. In most cases the residue was constituted by sufficiently pure divinyl diselenide. Purification was effected by washing with cold light petroleum or cold ethanol. Attempted chromatography on silica gel, deactivated silica gel or alumina columns gave rise to a product which was contaminated by some decomposition compounds. Analitically pure samples of (9c) and (10c) could not be obtained. The reaction yields and the physical and spectral data of the products obtained are reported below.

(Z)-β-Styryl diselenide, (9a), (82%), m.p. 72-4°C. ^{1}H-nmr δ 7.4 - 7.2 (m, 5H), 7.0 (d, 1H, J = 10 Hz), 6.85 (d, 1H, J = 10 Hz). ^{13}C-nmr δ 136.9 (ipso-C), 131.6 (α-vin-C), 128.5 (o-C), 128.4 (m-C), 127.7 (p-C), 126.3 (β-vin-C). Mass, m/e 364 (54), 284 (10), 205 (40), 182 (100). Anal. Calcd for $C_{16}H_{14}Se_2$: C, 52.76; H, 3.88. Found: C, 52.35; H, 3.98.

(E)-β-Styryl diselenide, (10a), (90%), m.p. 62-4°C. ^{1}H-nmr δ 7.3 - 7.15 (m, 5H), 7.15 (d, 1H, J = 16 Hz), 6.95 (d, 1H, J = 16 Hz). ^{13}C-nmr δ 136.9 (α-vin-C), 136.3 (ipso-C), 128.7 (o-C), 128 (p-C), 126.6 (m-C), 118 (β-vin-C). Mass, m/e 366 (50), 286 (34), 206 (64), 205 (62), 183 (100). Anal. Calcd for $C_{16}H_{14}Se_2$: C, 52.76; H, 3.88. Found: C, 53.00; H, 3.82.

(Z)-2-Phenylthio-1-ethenyl diselenide, (9b), (86%), m.p. 33-5°C. ^{1}H-nmr δ 7.45 - 7.2 (m, 5H), 7.1 (d, 1H, J = 8 Hz), 6.7 (d, 1H, J = 8 Hz). ^{13}C-nmr δ 134.8 (ipso-C), 129.5 and 129.2 (o-, m-, p-C), 127.1 (α-vin-C), 125.9 (β-vin-C). Mass, m/e 427 (9), 349 (13), 241 (40), 161 (100), 135 (35), 134 (54), 109 (65), 91 (26). Anal. Calcd for $C_{16}H_{14}S_2Se_2$: C, 44.86; H, 3.30. Found: C, 44.92; H, 3.36.

(E)-2-Phenylthio-1-ethenyl diselenide, (10b), (90%), oil. ^{1}H-nmr δ 7.4 - 7.15 (m, 5H), 6.85 (d, 1H, J = 15.5 Hz), 6.75 (d, 1H, J = 15.5 Hz). ^{13}C-nmr δ 133.6 (ipso-C), 132.6 (α-vin-C), 130.5 (o-C), 129.2 (m-C), 127.5 (p-C), 115.7 (β-vin-C). Mass, m/e 426 (9), 349 (5), 240 (16), 161 (100), 135 (48), 134 (62), 109 (44), 77 (11). Anal. Calcd for $C_{16}H_{14}S_2Se_2$:: C, 44.86; H, 3.30. Found: C, 45.02; H, 3.24.

(Z)-2-Phenylselenyl-1-ethenyl diselenide, (9c), (78%), oil. ^{1}H-nmr δ 7.6 - 7.35 (m, 2H), 7.45 (d, 1H, J = 8 Hz), 7.3 - 7.15 (m, 3H), 7.0 (d, 1H, J = 8 Hz). ^{13}C-nmr δ 132.1 (o-C), 130.2 (ipso-C), 129.3 (m-C), 128.9 (α-vin-C), 127.8 (β-vin-C), 127.5 (p-C).

(E)-2-Phenylselenyl-1-ethenyl diselenide, (10c), (72%), oil. ^{1}H-nmr δ 7.6 - 7.35 (m, 2H), 7.3 - 7.15 (m, 3H), 7.0 (d, 1H, J = 15.5 Hz), 6.8 (d, 1H, J = 15.5 Hz). ^{13}C-nmr δ 132.8 (o-C), 129.3 (m-C), 129.2 (ipso-C), 127.6 (p-C), 125.9 (α-vin-C), 118.4 (β-vin-C).

Decomposition of the Acyl Selenides with Sodium or with MeSNa.

To a solution of the acyl selenide (1 mmol) in DMF (6 ml), stirred under nitrogen at room temperature, the solution of sodium in HMPA or solid sodium methanethiolate (10% of the stoichiometric amount) was added. The progress of the reaction was followed by tlc. After 2 - 6 h the starting product was completely consumed and transformed into the corresponding diselenide. The reaction mixture was worked up as described above. In the case of MeSNa, (7a), (8a), and PhSeCOMe were converted in (9a), (10a) and diphenyl diselenide in 75, 72, and 85% yields, respectively; when the reactions were carried out with sodium in HMPA the corresponding reaction yields were 81, 82, and 88%. Under these latter conditions the (E)-PhCH=CHSeCOPh was transformed into (10a) in 78% yields.

Acknowledgment. This work was supported by a grant from the CNR program "Chimica Fine e Secondaria".

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7) The major product of the decomposition of the divinyl diselenide seems to be the corresponding divinyl selenide.
8) An alternative interpretation, which does not involve selenyl radicals as reactive intermediates, could be find assuming that the reaction of the vinyl selenide anion with iodine affords vinyl selenyl iodide which reacts with vinyl selenide anion to give the observed divinyl diselenide. More experimental data are necessary before the mechanistic aspects of these reactions can be clarified and we are presently working in this direction.
9) The first two steps are identical to those suggested in the Scheme 3. In the third step it is proposed that the electron transfer is effected by the vinyl selenide anions. As a matter of fact, in an independent experiment, it was observed that the conversion of (**7a**) into (**9a**) can also be induced by phenyl selenide anions.
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