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COMPETITION BETWEEN VINYLIC SUBSTITUTION AND CONJUGATE ADDITION IN THE REACTIONS OF VINYL SELENOXIDES AND VINYL SELENONES WITH NUCLEOPHILES IN DMF

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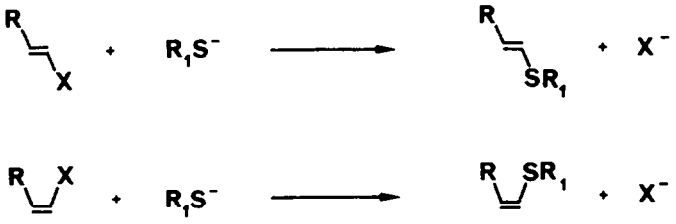
Abstract. Vinyl selenoxides and vinyl selenones present a different reactivity towards thiolate or alkoxide anions in DMF. In the case of selenoxides the addition of the nucleophiles regioselectively occurs at the α-carbon leading to the formation of the vinylic substitution products with complete retention of configuration. These reactions occur under very mild conditions indicating that the seleninyl group markedly enhances nucleophilic vinylic substitution rates. The results obtained with vinyl selenones are consistent with competitive nucleophilic attack at the α- and at the β-carbon. The former yields irreversibly the vinylic substitution products, whereas attack at the β-carbon leads to the reversible formation of selenonyl stabilized carbanions. The fate of these intermediates depends upon the nucleophilic reagent employed. With thiolate anions the vinyl selenones are rapidly subtracted from the equilibrium and the carbanion does not give any other product. With methoxide anions, on the contrary, the vinylic substitution is a slow process and the carbanion can give rise to conjugate addition products also. Malonate anions react only at the β-carbon of vinyl selenones and the resulting carbanions suffer proton transfer and intramolecular displacement of the selenonyl group to afford cyclopropane derivatives.

In a recent series of papers we have shown that selenium[1-3] and sulphur[4] nucleophiles, when used in dipolar aprotic solvents, easily effect stereospecific nucleophilic vinylic substitution reactions on unactivated vinyl halides. These reactions represent very simple and useful syntheses of vinyl alkyl and vinyl aryl selenides and sulphides which are convenient precursors of several organic compounds.[1-4] Sulphur anions in DMF are strong nucleophiles and we have observed that they effect vinylic substitutions even on vinyl alkyl or aryl sulphides and selenides[5] (Scheme 1). In no case stereospecific vinylic substitutions by oxygen nucleophiles could be effected. All these reactions occurred with complete retention of configuration and have been interpreted as bimolecular substitutions which involve nucleophilic attack at the vinylic carbon atom holding the leaving Cl, Br, SR and SeR groups (Addition-elimination mechanism[6,7]).

These investigations have now been extended to vinyl selenoxides and vinyl selenones which exhibit characteristic features in their reactions with nucleophiles. The seleninyl and selenonyl

SCHEME 1



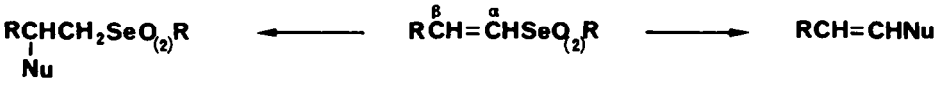
R = Ph, PhS, PhSe

R_1 = Me, Me_2CH, Ph

X = Cl, Br, SMe, $SCHMe_2$, SeMe, SePh

groups are strong electron-attracting groups and thus they activate the carbon-carbon double bond towards the addition of nucleophiles at the β-carbon;[8] at the same time, when linked to a saturated carbon these two substituents act as very good leaving groups.[8,9] It seems reasonable to assume that the RSeO and $RSeO_2$ can behave as good leaving groups in nucleophilic vinylic substitutions also, provided appropriate reaction conditions are employed. Thus, in principle, the reaction of a nucleophile (Nu) with vinyl selenoxides and selenones can proceed in two different ways, i.e. addition at the β-carbon to give the product of conjugate addition or addition at the α-carbon to give the product of vinylic substitution (Scheme 2).

SCHEME 2

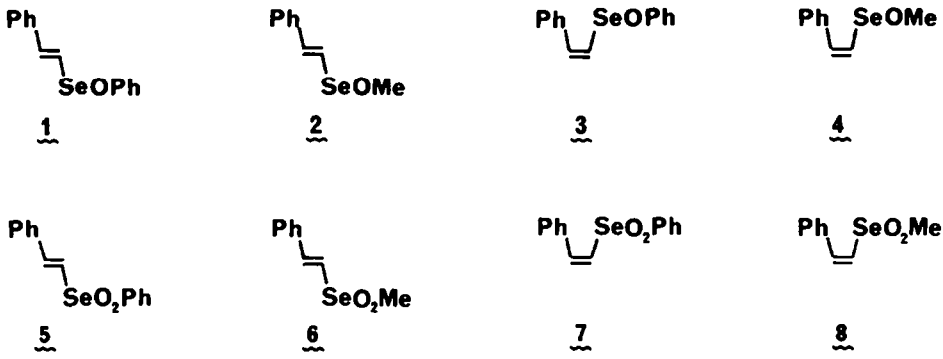


In previous works only the first process has been observed;[8] dipolar aprotic solvents however were never employed. It can be expected that the course of these reactions will be influenced, not only by the nature of the nucleophile, but also by the properties of the solvent employed. On the basis of these considerations we have undertaken an investigation with the aim of finding information about the factors governing the regioselectivity of the addition of nucleophiles to vinyl selenoxides and selenones. The results reported in this paper concern the reactions carried out with sodium methanethiolate, sodium methoxide and sodium methyl malonate in dimethylformamide. The same reactions carried out in protic solvents give different results.[10]

RESULTS AND DISCUSSION

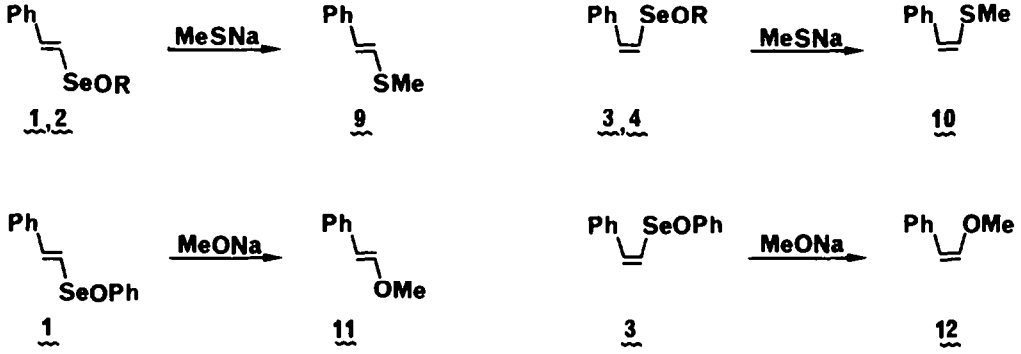
The substrates employed for the present investigations were the (E)- and (Z)-β-styryl methyl or phenyl selenoxides 1 - 4 and selenones 5 - 8 which can be obtained by oxidation of the corresponding selenides with m-chloroperbenzoic acid (MCPBA). Compounds 1 - 6 were obtained in good yields, whereas the (Z)-selenones 7 and 8 were formed in moderate yields even with a large excess of MCPBA and at higher temperatures; considerable amounts of the selenoxides 3 and 4 remained in the reaction mixtures.

The reactions of the selenoxides with 2 molar equivalents of MeSNa proceeded smoothly at room temperature and were complete few minutes after the mixing of the reagents; a single product was obtained in every case. Compounds 1 and 2 afforded the (E)-β-styryl methyl sulphide 9 in 82 and



94% yield, and compounds 3 and 4 gave the (Z)-β-styryl methyl sulphide 10 in 78 and 89% yield, respectively (Scheme 3). The reactions occurred with complete retention of configuration.

SCHEME 3



These reactions represent therefore new interesting examples of nucleophilic vinylic substitutions which occur on substrates which are not activated by the presence of a strong electron-withdrawing substituent in the β-carbon atom. In respect to the previously described reactions, carried out on vinyl halides, sulphides and selenides,[1-5] the reaction conditions employed for the vinyl selenoxides are much milder. Thus, the addition of a nucleophile at the α-carbon atom, which in unactivated substrates is very likely the rate determining step of the vinylic substitution reactions occurring with the addition-elimination mechanism,[1,4] is greatly accellerated by the presence of the strong electron-attracting ArSeO group. Similar activation by electronegative substituents in the α-position has already been observed in other vinylic substrates.[7]

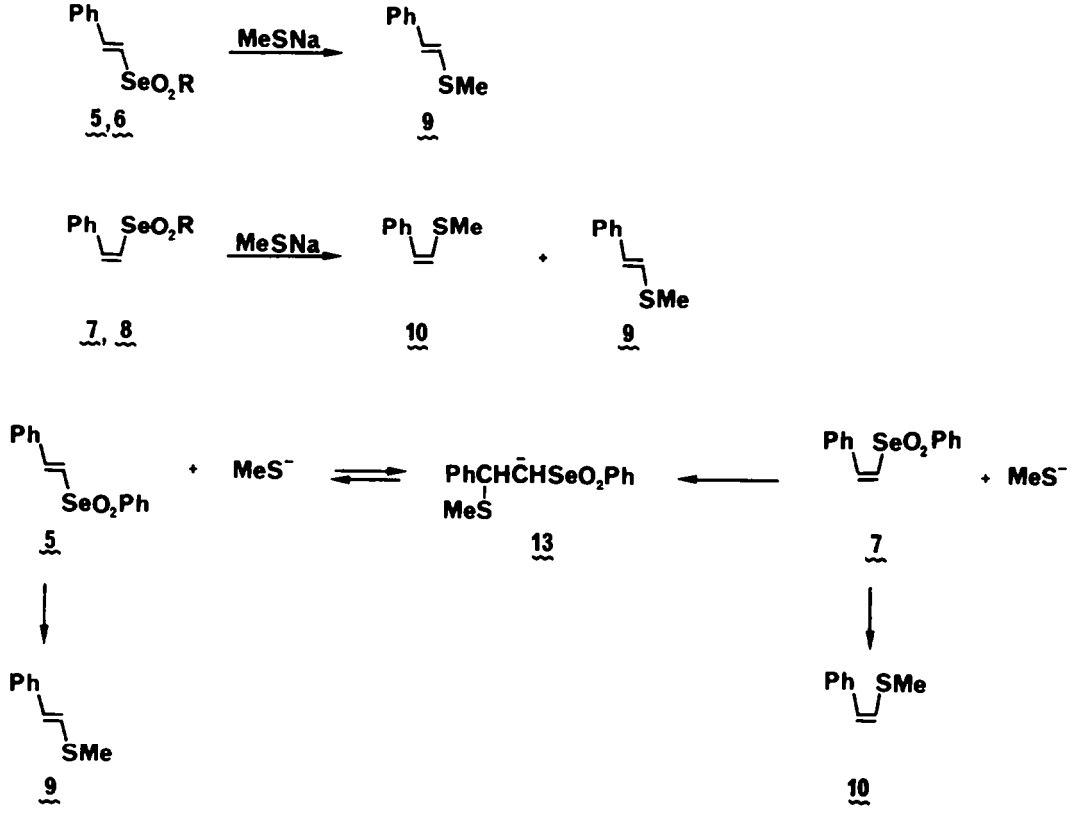
The high reactivity of vinyl selenoxides should make possible to effect stereospecific nucleophilic vinylic substitutions even with a weak nucleophile such as the alkoxide ion. Indeed, the reaction of 1 with excess MeONa (4 molar equivalents), in DMF at room temperature for 4 h, afforded the (E)-β-methoxystyrene 11 in 80% yield; under the same conditions the (Z)-isomer 3 gave the (Z)-β-methoxystyrene 12 in 60% yield (Scheme 3). This is the first example of a stereospecific vinylic substitution effected by an oxygen nucleophile on unactivated systems. Under more severe experimental conditions vinylic substitution by methoxide ions took place with vinyl halides also.[4] In that case however the reactions were stereoconvergent and not stereospecific and a different mechanism was operating. It has been shown in fact that the substitution products were the result of an elimination-addition mechanism, involving the attack of the methoxide ion at the β-hydrogen to give the elimination product; the addition of the methoxide ions to the

phenylacetylene thus formed gave rise to a mixture of the (E)- and (Z)-β-methoxystyrenes.[4]

Thus, using vinyl selenoxides as substrates and working in dipolar aprotic solvents, nucleophilic substitutions can be easily effected both with thiolate and alkoxide anions; obviously in the latter case the process is much slower and it requires longer reaction times. The reactions of MeSNa and MeONa with vinyl selenoxides in DMF are completely regiospecific; no evidences could in fact be found indicating that the addition can occur at the β-carbon atom also.

A different picture emerges from the results of the reactions of MeSNa and MeONa with the vinyl selenones 5-8. The reactions of the (E)-selenones 5 and 6 with sodium methanethiolate (2 molar equivalents) in DMF gave cleanly the (E)-β-styryl methyl sulphide 9 in 95 and 90% yield, respectively, whereas the (Z)-selenones 7 and 8 gave rise to an almost equimolecular mixture (75 and 73% yield) of the two isomeric substitution products 9 and 10 (Scheme 4). In this case also the reactions were extremely fast, the starting selenones being completely consumed just after the addition of the MeSNa at room temperature.

SCHEME 4



Since the (Z)-sulphide 10 does not isomerize to 9 under the reaction conditions employed, very likely the isomerization occurs in the starting selenones. Indeed, the selenone 7, when dissolved in DMF remains unchanged, whereas if small amounts of MeSNa are added a mixture of 7 and 5, together with some 9 and 10, is obtained. The experimental results obtained can be explained as indicated in Scheme 4 for the styryl phenyl selenones 5 and 7.

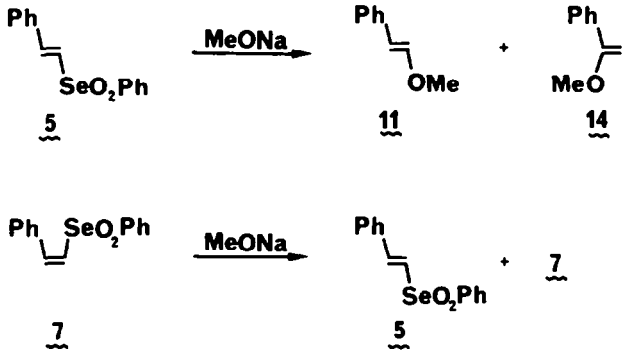
Two competitive reactions are taking place with comparable rates, i.e. the addition of the MeS anion at α-carbon which irreversibly gives the vinylic substitutions products 9 and 10 with retention of configuration, and the addition at the β-carbon which reversibly gives the anion 13.

Since the reaction medium is aprotic, the anion 13 can only evolve by eliminating the MeS anion thus reverting to the vinyl selenones. The (E)-selenone 5 is very likely thermodynamically much more stable than (Z)-isomer 7 and therefore 13 evolves exclusively towards 5; as a matter of fact 7 is not formed at all when 5 is treated with small amounts of MeSNa in DMF. Thus, when the reaction is carried out on 5 the only observable process is the nucleophilic vinylic substitution to give 9; the addition at the β-carbon is obviously occurring also but it has no practical consequences. On the contrary, when the (Z)-selenone 7 is treated with MeSNa, the addition at the α-carbon stereoselectively gives 10 and the addition at the β-carbon produces the isomerization of 7 into 5; as a consequence a mixture of 9 and 10 is obtained.

These results demonstrate that, beside vinyl selenoxides, vinyl selenones also easily give rise to stereospecific nucleophilic vinylic substitutions in dipolar aprotic solvents. However, the selenonyl is very likely a more powerful electron-attracting group than the seleninyl and not only does it makes the addition at the α-carbon easier but it also activates the carbon-carbon double bond towards the addition of nucleophiles at the β-position.

The results obtained from the reactions of vinyl selenones with sodium methoxide can be explained in a similar way and supply further evidences which support the proposed ambidentic behaviour of vinyl selenones. The reaction of the (E)-β-styryl phenyl selenone 5 with MeONa (4 molar equivalents), in DMF at room temperature for 15 minutes, afforded the (E)-β-methoxystyrene 11 (48%) together with a second product (25%) which was identified as the α-methoxystyrene 14. The ratios of the two products was influenced by the amount of the MeONa employed, as well as by the reaction temperature. Under similar conditions the (Z)-isomer 7 was extensively isomerized to the (E)-selenone 5 (Scheme 5).

SCHEME 5

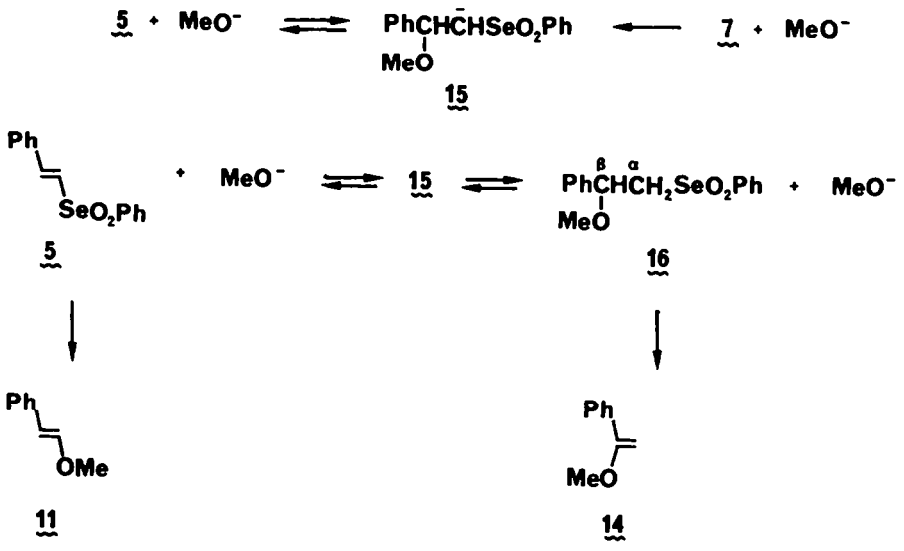


Addition of methoxide anions at the β-carbon to give the anion 15 is clearly responsable for the isomerization of the (Z)-selenone 7 into the more stable (E)-selenone 5 (Scheme 6). Addition at the α-carbon produces the substitution product 11. Thus the two competitive addition processes are taking place with methoxide ions also. In this case, however, owing to the lower nucleophilicity of the MeO anion in respect to the MeS anion, the vinylic substitution, i.e. the addition at the α-carbon, is a much slower process.

The carbanion 15 therefore, besides reverting to 5, can also abstract a proton from the medium to afford the conjugate addition product 16. Methoxide anions react with this latter product either by abstracting the α-proton to give 15 or by attacking the β-proton and eliminating the selenonyl group to give the observed reaction product 14. The product of nucleophilic displacement of the selenonyl group,[10] $PhCH(OMe)CH_2OMe$, was not observed; the methoxide ion, in fact, in dipolar aprotic solvents, more than as a nucleophile, behaves as a strong base.[10,11] This

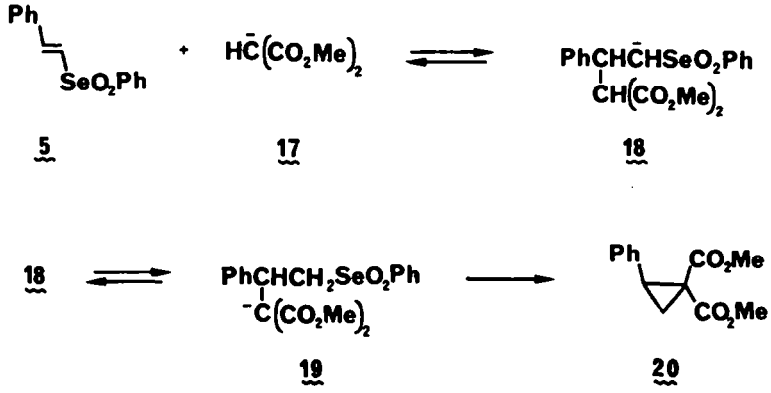
interpretation is corroborated by the fact that the presence of compound **16** in the reaction mixture can be demonstrated by ^{1}H-nmr when the reaction is stopped before completion. Besides, the proposed mechanism reported in Scheme 6 implies that if compound **16** is allowed to react with sodium methoxide in DMF one should again obtain a mixture of the two products **11** and **14**. This has been experimentally confirmed. Thus, with the strongly nucleophilic thiolate anions the only observed process is the vinylic substitution, whereas with methoxide anions products deriving from addition at the α- and at the β-carbon are both observed. The use of other anionic species in

SCHEME 6



aprotic solvents can give rise to products deriving from addition at the β-carbon exclusively. Indeed, it has already been reported in the literature that in tetrahydrofuran vinyl selenones react with anionic species of active methylene compounds[8,12,13] to give the carbanions deriving by addition at the β-carbon; interestingly, these intermediates give rise to proton transfer followed by intramolecular displacement of the $ArSeO_2$ group to eventually afford cyclopropane derivatives. We have observed that a similar reaction occurs in DMF when the selenone **5** is treated with sodium methyl malonate **17** (Scheme 7). In this case no trace of the vinylic substitution product could be

SCHEME 7



observed, the only reaction product being the cyclopropane **20** (70% yield). A reaction sequence, identical to that proposed for the similar reactions carried out in THF[8] and involving the

intermediate formation of carbanions **18** and **19**, can be suggested to be operating in the present case also (Scheme 7).

The observed behaviour of vinyl selenoxides and vinyl selenones towards sodium thiolate and sodium methoxide is due to the nature of the solvent employed which greatly enhances the reactivity of anions by specific solvation of the cation. If protic solvents are employed the nucleophilicity of MeS and MeO anions is greatly decreased and the vinylic substitution on unactivated substrates usually does not occur.[4] Under these conditions therefore the only observable process with vinyl selenones should be the attack at the β-carbon leading to the formation of the conjugate addition products.[10] Similar changes in positional selectivity on passing from protic to dipolar aprotic solvents have already been observed in the reactions of nitroalkenes with CN anions.[14]

EXPERIMENTAL

Structural attributions were made by proton, carbon-13 nmr spectra and by elemental analyses. Proton nmr spectra were recorded at 90 MHz on a Varian EM 390 instrument ($CDCl_3$ solutions, TMS as reference). Carbon-13 nmr spectra were recorded at 20.15 MHz on a Bruker WP 80 SY instrument operating in Fourier transform mode with proton decoupling throughout. 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 20 in., 3% UCW 982 column. (Z)- and (E)-β-styryl methyl selenides,[3] (Z)- and (E)-β-styryl phenyl selenides[3] and (Z)- and (E)-β-styryl methyl sulphides[4] **9** and **10** were prepared as described in previous works. Commercial sodium methanethiolate and methoxide were used without further purification.

Synthesis of Vinyl Selenoxides and Vinyl Selenones.

The oxidation of the selenides (10 mmol) was effected with MCPBA (1.3 and 2.6 molar equivalents for the selenoxides and the selenones, respectively); K_2HPO_4 (2.5 and 4.5 molar equivalents, respectively) was also added in some cases (Compounds **1**, **3**, **5**, **7**). The progress of the reaction was monitored by tlc. The reaction mixture was poured on 10% Na_2CO_3 solution and extracted with chloroform. The organic layer was washed with 10% Na_2CO_3 solution and with water, dried and evaporated. The residue was chromatographed through a deactivated silica gel column using a mixture of chloroform and methanol (95:5) as eluant. With the exception of compound **1** the selenoxides were hygroscopic solids (m.p. not determined); the selenones were stable white crystalline compounds. The physical and spectral data of the products obtained are reported below; the solvent employed, the reaction temperature, the reaction time and the yields are given in the order in parentheses.

(E)-β-Styryl phenyl selenoxide, **1**, (THF, 0°C, 5 h, 78%), m.p. 100-101°C. ^{1}H-nmr δ 7.85 - 7.65 (m, 2 H), 7.55 - 7.4 (m, 4 H), 7.35br (s, 5 H), 7.1 (d, 1 H, J = 16 Hz). ^{13}C-nmr δ 138.7, 131.4, 129.9, 129.8, 128.9, 127.8, 126.4. Anal. Calcd for $C_{14}H_{12}OSe$: C, 61.09; H, 4.40. Found: C, 61.20; H, 4.35.

(E)-β-Styryl methyl selenoxide, **2**, (CH_2Cl_2, 0°C, 0.5 h, 75%). ^{1}H-nmr δ 7.55 - 7.15 (m, 7 H), 2.65 (s, 3 H). ^{13}C-nmr δ 138.6 (vin-C), 133.7 (vin-C), 129.7 (p-C), 129.3 (ipso-C), 128.8 and 127.6 (o- and m-C), 35.1 (Me). Anal. Calcd for $C_9H_{10}OSe$: C, 50.71; H, 4.74. Found: C, 50.60; H, 4.69.

(Z)-β-Styryl phenyl selenoxide, **3**, (THF, 0°C, 1 h, 75%). ^{1}H-nmr δ 7.85 - 7.55 (m, 2 H), 7.55 - 7.3 (m, 8 H), 7.25 (d, 1 H, J = 10 Hz), 6.55 (d, 1 H, J = 10 Hz). ^{13}C-nmr δ 140.8, 137.0, 134.4, 131.1, 129.6, 129.5, 128.8, 126.1. Anal. Found: C, 61.05; H, 4.43.

(Z)-β-Styryl methyl selenoxide, **4**, (CH_2Cl_2, 0°C, 1 h, 72%). ^{1}H-nmr δ 7.5 - 7.3 (m, 5 H), 7.25 (d, 1 H, J = 10 Hz), 6.65 (d, 1H, J = 10 Hz), 2.65 (s, 3 H). Anal. Found: C, 50.73; H, 4.70.

(E)-β-Styryl phenyl selenone, **5**, (MeOH, 25°C, 6 h, 90%), m.p. 92-4°C. ^{1}H-nmr δ 8.15 - 8.0 (m, 2 H), 7.85 (d, 1 H, J = 15.5 Hz), 7.7 - 7.2 (m, 9 H); (C_6D_6) δ 8.15 - 7.95 (m, 2 H), 7.85 (d, 1 H, J = 15.5 Hz), 7.65 (d, 1 H, J = 15.5 Hz), 7.35 - 7.0 (m, 8 H). ^{13}C-nmr δ 145.3, 134.1, 131.8, 130.3, 129.3, 128.8, 127.8, 126.9. Anal. Calcd for $C_{14}H_{12}O_2Se$: C, 57.74; H, 4.16. Found: C, 57.43; H, 4.06.

(E)-β-Styryl methyl selenone, **6**, (MeOH, 0°C, 3 h, 91%), m.p. 137-9°C. ^{1}H-nmr δ 7.8 (d, 1 H, J = 15.5 Hz), 7.65 - 7.4 (m, 5 H), 7.3 (d, 1 H, J = 15.5 Hz), 3.35 (s, 3 H). ^{13}C-nmr δ 145.5 (vin-C), 132.0 (vin-C), 131.5 (ipso-C), 129.3 and 128.8 (o- and m-C), 127.9 (p-C), 43.8 (Me). Anal. Calcd for $C_9H_{10}O_2Se$: C, 47.17; H, 4.41. Found: C, 47.30; H, 4.37.

(Z)-β-Styryl phenyl selenone, **7**, (THF, 70°C, 8 h, 46%), m.p. 96-8°C. ^{1}H-nmr δ 7.85 - 7.1 (m, 11 H), 6.8 (d, 1 H, J = 10.5 Hz). ^{13}C-nmr δ 145.3 (vin-C), 142.5, 133.7 (vin-C), 132.4, 131.7, 130.6, 129.8, 129.7, 128.4, 126.7. Anal. Found: C, 57.80; H, 4.19.

(Z)-β-Styryl methyl selenone, **8**, (MeOH, 25°C, 12 h, 42%), m.p. 103-5°C. ^{1}H-nmr δ 7.9 - 7.7 (m, 2 H), 7.65 - 7.3 (m, 4 H), 6.75 (d, 1 H, J = 10.5 Hz), 3.0 (s, 3 H). Anal. Found: C, 47.27; H, 4.46.

Reactions of selenoxides 1 - 4 with MeSNa or MeONa in DMF.

The selenoxide (5 mmol) was dissolved in DMF (15 ml) and MeSNa (2 mmol) or MeONa (4 mmol) was

added. The progress of the reaction was monitored by tlc. In the case of MeSNa the reaction was immediate, whereas in the case of MeONa the reactions were complete after 4 h. After the usual work up the reaction products were separated and purified by column chromatography on silica gel using light petroleum as eluant. Reaction products and yields are reported under the Results and Discussion section. The sulphides **9** and **10** were already described.[4] The physical and spectral data of the products obtained with MeONa are reported below.

(E)-β-Methoxystyrene, **11**, oil. ^{1}H-nmr δ 7.2br (s, 5 H), 6.95 (d, 1 H, J = 13 Hz), 5.7 (d, 1 H, J = 13 Hz), 3.7 (s, 3 H). These data correspond to those reported in the literature.[15]

(Z)-β-Methoxystyrene, **12**, oil (Lit.[16] b.p. 44°C/0.3 mm). ^{1}H-nmr δ 7.7 - 7.1 (m, 5 H), 6.15 (d, 1 H, J = 7 Hz), 5.2 (d, 1 H, J = 7 Hz), 3.75 (s, 3 H). These data correspond to those reported in the literature.[16]

Reactions of selenones 5 - 8 with MeSNa or MeONa in DMF.

The selenone (5 mmol) was dissolved in DMF (15 ml) and MeSNa (2 mmol) or MeONa (4 mmol) was added. The reactions were complete few minutes after mixing of the reagents. The reactions were worked up as described above for the selenoxides. Reaction products and yields are reported under the Results and Discussion section. The α-methoxystyrene **14**, by column chromatography on silica gel, is partially converted into acetophenone; the mixture deriving from the reaction with MeONa was therefore chromatographed through a deactivated alumina column. The physical and spectral data of compounds **9** and **10** were already reported in the literature,[4] and those of compound **11** are described above. The data of compound **14** are reported below.

α-Methoxystyrene, **14**, oil (Lit.[17] b.p. 85-7°C/13 mm). ^{1}H-nmr δ 7.6 - 7.35 (m, 2 H), 7.25 - 7.05 (m, 3 H), 4.55 (d, 1 H, J = 3 Hz), 4.15 (d, 1 H, J = 3 Hz), 3.7 (s, 3 H). These data correspond to those reported in the literature.[17]

Reaction of (E)-β-styryl phenyl selenone 5 with sodium methyl malonate.

Sodium hydride (5 mmol) was added at room temperature to a solution of methyl malonate (5 mmol) in DMF (15 ml). The selenone **5** (5 mmol) was added and the mixture was stirred at room temperature for 8 h. The progress of the reaction was monitored by tlc. The mixture was poured on water and extracted with ether. The ether was washed with water, dried and evaporated. The residue was constituted by almost pure **20** (^{1}H-nmr, tlc). Purification was effected by column chromatography on silica gel using a mixture of light petroleum and ether (85 : 15) as eluant.

Dimethyl 2-Phenyl-1,1-cyclopropanedicarboxylate, **20**, oil. ^{1}H-nmr δ 7.2br (s, 5 H), 3.8 (s, 3 H), 3.35 (s, 3 H), 3.25 (dd, 1 H, J = 9.3 and 8.1 Hz), 2.15 (dd, 1 H, J = 8.1 and 5.1 Hz), 1.75 (dd, 1 H, J = 9.3 and 5.1 Hz). ^{13}C-nmr δ 170.2 (CO), 170.0 (CO), 134.6 (ipso-C), 128.5 and 128.1 (o- and m-C), 127.4 (p-C), 52.7 (Me), 52.1 (Me), 37.2 (C-1), 32.5 (C-2), 19.0 (C-3). These attributions were made by off-resonance experiments. Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.64; H, 6.04. Found: C, 66.80; H, 6.15.

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