Tetrahedron Vol. 42, No. 17, pp. 4897 to 4906, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00

FORMATION AND REACTIVITY OF THE ADDITION PRODUCTS OF ALKOXIDES AND THIOLATE ANIONS TO VINYL SELENONES

MARCELLO TIECCO,* DONATELLA CHIANELLI, MARCO TINGOLI, LORENZO TESTAFERRI and DONATELLA BARTOLI

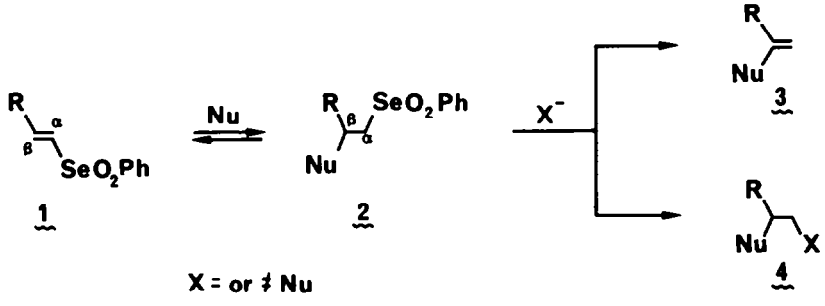
Istituto di Chimica Organica, Facoltà di Farmacia, Università di Perugia, Italy.

(*Received in UK* 13 *June* 1986)

Abstract. Vinyl selenones react with sodium methanethiolate in methanol to give the product of conjugate addition and subsequent displacement of the selenonyl group. On the contrary, the same reaction carried out with alkoxide anions affords the conjugate addition products in excellent yields. These β-alkoxy alkyl phenyl selenones are stable compounds which can react in several ways with loss of the selenonyl group. Their reactions with MeONa or MeSNa have been investigated both in MeOH and in DMF. The products observed derive from substitution and elimination processes as well as from retro Michael reactions followed by nucleophilic substitution of the vinyl selenone thus generated. These results indicate that the $ArSeO_2$ is a strong electron attracting group with peculiar properties. Beside making acidic the α-hydrogen atoms it activates the carbon-carbon double bond towards the addition of anionic reagents and it acts as a good leaving group in nucleophilic substitution, both aliphatic and vinylic, and in elimination reactions. The appropriate choice of the reagent and of the solvent allows to direct the reaction towards the desired products. Useful synthetic applications of these reactions are presented.

We have previously observed that vinyl selenoxides react with sodium methanethiolate and sodium methoxide, in dipolar aprotic solvents, to afford the products of nucleophilic vinylic substitution.[1] These reactions are stereospecific and occur much more easily than those with other unactivated substrates like vinyl halides,[2,3] sulphides and selenides.[4] Under the same conditions vinyl selenones 1 present an ambidentic behaviour giving rise to competitive additions at the α- as well as at the β-carbon atoms. However, since the reaction medium employed was aprotic (DMF), the conjugate addition products could not be isolated; their formation as intermediates was inferred from the observed isomerization of the starting selenones as well as from the structure of some of the reaction products.[1,5] Similar addition products were also formulated as intermediates in the reactions of further functionalized vinyl selenones with other anionic species; these compounds however were not isolated because, under the conditions employed, they were rapidly consumed to give the products of intermolecular or intramolecular displacement of the selenonyl group.[6-9]

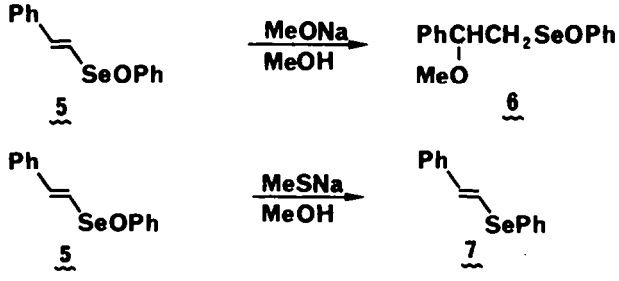
The reactions of vinyl selenoxides and vinyl selenones with RONa and MeSNa have been now investigated in protic solvents. Under these conditions the nucleophilicity of the oxygen and sulphur anions is greatly decreased and the vinylic substitution does not occur. With the vinyl selenones 1 the only process observed is the addition of the nucleophile (Nu) at the β-carbon to give the conjugate addition products 2. When alkoxide anions are employed compounds 2 (Nu = OR) can be isolated in good yields. The aryl alkyl selenones 2 give rise to several reactions. Depending on the nature of the anionic species (X^-) and on the reaction medium employed, one can observe the abstraction of the α-proton to give the vinyl selenone 1, the attack at the β-proton with loss of the selenonyl group to give products 3, and the attack at the α-carbon to give the substitution products 4;[10] with nucleophiles having particular structures this substitution can occur intramolecularly to afford cyclic products. We describe in this paper the synthesis of compounds 2 and their reaction with MeONa and MeSNa in MeOH and in DMF. The results obtained in DMF support the previously proposed interpretation of the behaviour of vinyl selenones with nucleophiles in dipolar aprotic solvents.[1]



RESULTS AND DISCUSSION

From the reaction of the (E)-β-styryl phenyl selenoxide 5 with MeONa in MeOH the presence of minute amounts of the addition product 6 could be evidenced by ^{1}H-nmr analysis of the reaction mixture; most of the starting product remained unchanged (Scheme 1). No conditions could be found

SCHEME 1

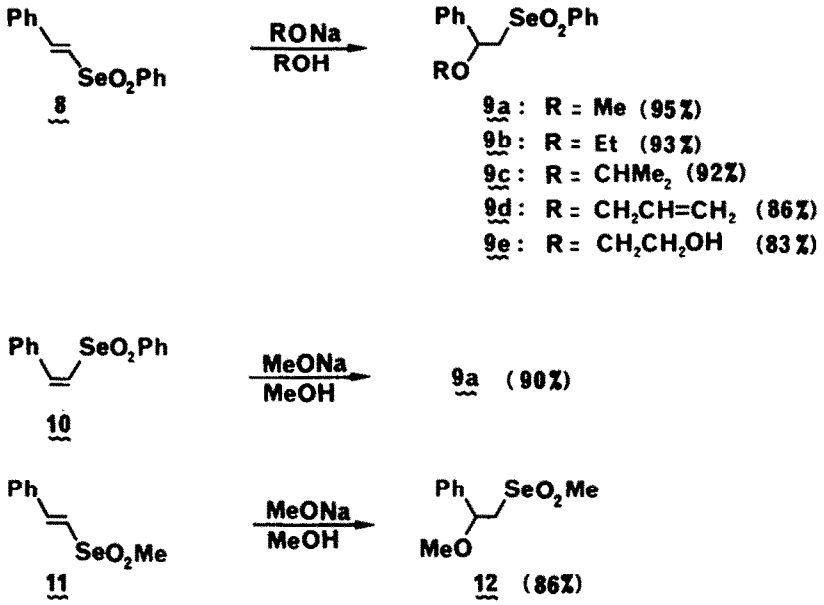


to improve the yields of compound 6.[11] The reaction with MeSNa took a completely different course giving rise exclusively to the deoxygenated product 7.

On the contrary, when the (E)-β-styryl phenyl selenone 8 was treated with MeONa in MeOH, in an ice bath, a precipitate was formed which was identified as the Michael addition product 9a. In a similar way, from the reaction of other alkoxide anions in the corresponding alcohols, high yields of the addition products could be obtained (Scheme 2). Compound 9a was also obtained from the

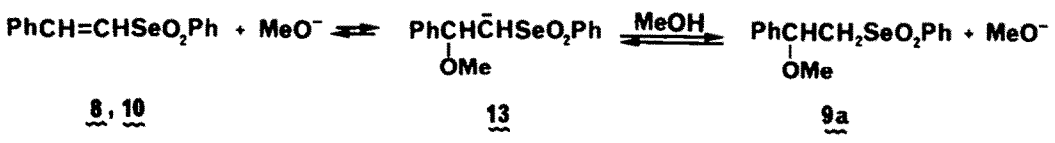
(Z)-isomer 10. The addition product 12 was formed from the reaction of the (E)-β-styryl methyl selenone 11 with MeONa in MeOH. These are the first examples in which the conjugate addition

SCHEME 2



products of an anionic species to vinyl selenones could be isolated. The course of these reactions is straightforward and is reported in Scheme 3 in the case of the addition of sodium methoxide in methanol:

SCHEME 3

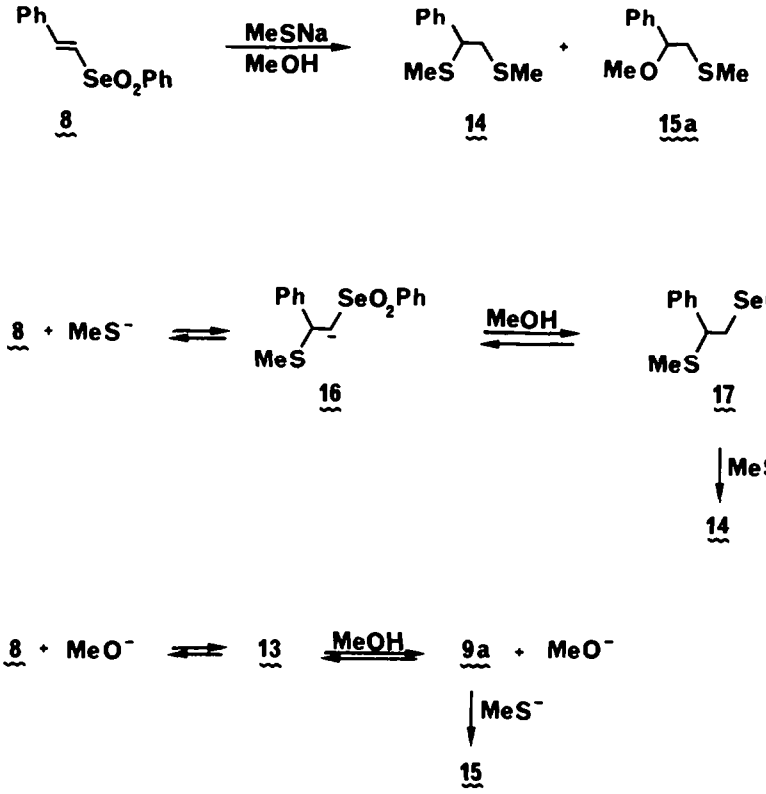


This mechasnism suggests that alkoxide ions are needed as catalysts only and that the process is reversible. Indeed, compound 9a was obtained equally well also in the case in which only catalytic amounts of MeONa were employed. Besides, since compounds 9 are substracted by precipitation, the equilibrium is completely shifted to the right. Further evidences for the reversibility of the process will be discussed below. Compounds 9 can also be obtained by oxidation of the corresponding selenides.[12]

The reaction of the vinyl selenone 8 with sodium methanethiolate (2 molar equivalents) in MeOH at 0°C was complete in 1 h. The reaction mixture was constituted by two products which were identified as the 1,2-bis(methylthio)phenylethane 14 (35%) and the 1-phenyl,1-methoxy,2-methylthioethane 15a (38%) (Scheme 4). The formation of these two products can be rationalized as indicated in Scheme 4. Addition of the MeS anion to 8 gives the carbanion 16 which abstracts a proton from the solvent to give methoxide anions and the addition product 1-methylthio,2-phenylselenonyl,1-phenylethane 17. This aryl alkyl selenone however cannot be isolated since, in the presence of a strong nucleophile such as the MeS anion, it is rapidly

consumed to give the substitution product **14**. On the other hand, as it has been shown above (Scheme 3) the methoxide ions react easily with **8** to give the addition product **9a**; this selenone, like **17**, reacts with MeS^- to give the observed product **15a**. Thus, whereas the MeS^- is consumed in

SCHEME 4



the substitution reactions of **17** and **9a**, the MeO^- is only involved in the reaction with **8**; this is a catalytic process from which methoxide ions are continuously regenerated.

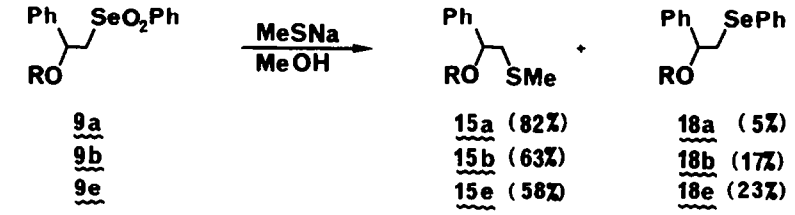
The results reported in Schemes 3 and 4 seem to indicate that the thiolate anions react faster with the alkyl aryl selenones **17** and **9a** than with the vinyl selenone **8**, whereas the methoxide anions react faster with **8** than with **17** and **9a**; as a matter of fact, under the conditions employed, products deriving from the reaction of **17** and **9a** with MeO^- could not be observed. Thus, from the reaction of **8** with MeSNa in MeOH, the conjugate addition products **17** and **9a** cannot be isolated since they are rapidly consumed by the MeS^- and in the other hand the formation of products deriving by the addition of methoxide ions to **8** cannot be avoided. In order to suppress this latter undesired process it is necessary to work under conditions in which all the starting vinyl selenone is consumed by the reaction with the methanethiolate anion. Indeed when the reaction was carried out with a large excess of MeSNa (10 molar equivalents) compound **14** (70%) was isolated as the sole reaction product. The reactions of both MeS and RO anions with vinyl selenones in protic solvents are completely regioselective; no products deriving from the addition of the nucleophiles at the α-carbon atom could be observed. Attack at the α- and at the β-carbon atoms are instead in competition when dipolar aprotic solvents are employed.[7]

Krief and coworkers[10] have recently reported that alkyl phenyl selenones readily undergo substitution reactions with a variety of nucleophiles including MeONa in MeOH and PhSNa in

ethanol. We have examined the behaviour of the β-alkoxyalkyl phenyl selenones 9 towards MeONa and MeSNa in MeOH and in DMF. Some information were already available from the reactions described above (Scheme 4) in which the aryl alkyl selenones were proposed to intervene as intermediates.

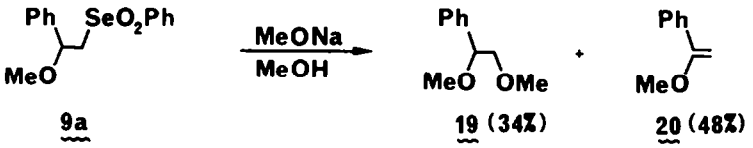
The reactions of compounds 9 with MeSNa (2 molar equivalents), in methanol at room temperature, afforded the expected substitution products 15 together with some deoxygenated compounds 18 (Scheme 5). The relative amounts of the two products changed with the nature of the alkoxy group. Apart from this side reaction, the predominant process observed in this case is the attack of the nucleophile at the α-carbon of the aryl alkyl selenone to give the substitution products. The

SCHEME 5

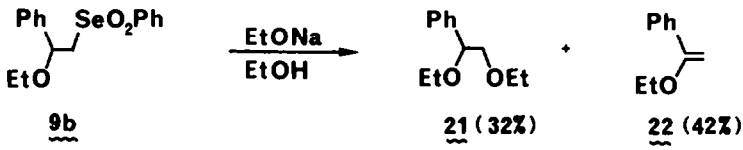


9a 15a (82%) 18a (5%)
9b 15b (63%) 18b (17%)
9e 15e (58%) 18e (23%)

a: R = Me b: R = Et e: R = CH_2CH_2OH



9a 19 (34%) 20 (48%)



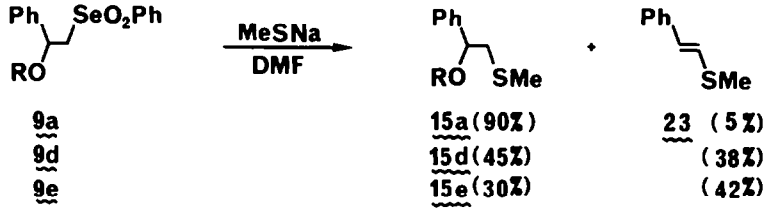
9b 21 (32%) 22 (42%)

reactions with alkoxide anions in alcohols were slower (8 - 10 h) and took a different course. Thus from the reaction of 9a with MeONa (4 molar equivalents) the substitution product 19 was accompanied by a second compound which was identified as the α-methoxystyrene 20. A similar mixture of two products 21 and 22 was obtained from the reaction of 9a with EtONa in EtOH (Scheme 5). These two reactions can also be carried out, with quite similar results, starting directly from the vinyl selenone 8 and using 5 molar equivalents of MeONa or EtONa. In this case therefore the attack at the α-carbon and at the β-hydrogen, i.e. the substitution and the elimination reactions are in competition. The attack at the α-proton to give the carbanion 13 is also taking place but it has no practical consequences. The same reaction carried out on the n-decyl phenyl selenone gave only the product of the substitution of the $ArSeO_2$ group;[10] the particular structure of the alkyl moiety in the selenones 9 is probably responsable for the occurrence of the elimination reaction.

The reactivity of the selenones 9 changed on passing from methanol to DMF. From the reactions with MeSNa (0°C, 0.5 h), together with the substitution products a second compound, identified as the (E)-β-styryl methyl sulphide 23, was isolated; the relative amounts of the two products

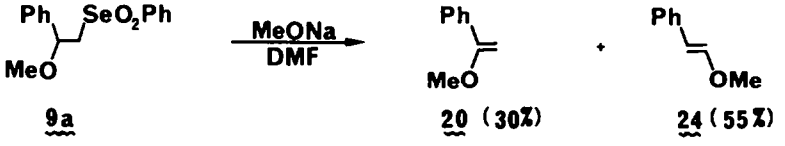
changed with the bulkiness of the alkyl group R in the starting selenones 9 (Scheme 6). The reaction of 9a with MeONa (0°C, 0.5 h) did not give any substitution product 19; the reaction mixture was constituted by the α-methoxystyrene 20 and the (E)-β-methoxystyrene 24. These results confirm previous observations that alkoxide anions in DMF more than as nucleophiles behave as strong bases.[1,13]

SCHEME 6



9a 15a (90%) 23 (5%)
9d 15d (45%) (38%)
9e 15e (30%) (42%)

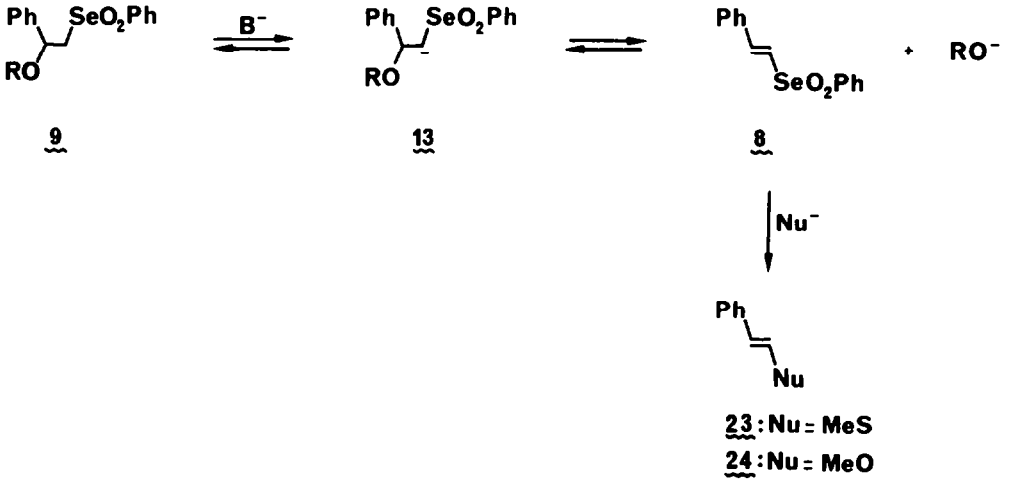
a : R = Me d : R = $CH_2CH{=}CH_2$ e : R = CH_2CH_2OH



9a 20 (30%) 24 (55%)

The formation of compounds 23 and 24 clearly indicates that in DMF a retro Michael reaction takes place to afford the (E)-β-styryl phenyl selenone 8 (Scheme 7) which suffers nucleophilic vinylic substitution by the MeS or the MeO anions.[1] This reaction proceeds easily since, in DMF, the abstraction of a proton from the solvent by the anion 13 is difficult and the selenone 8 can be subtracted from the equilibrium by irreversible addition of nucleophiles at the α-position.[1] This

SCHEME 7



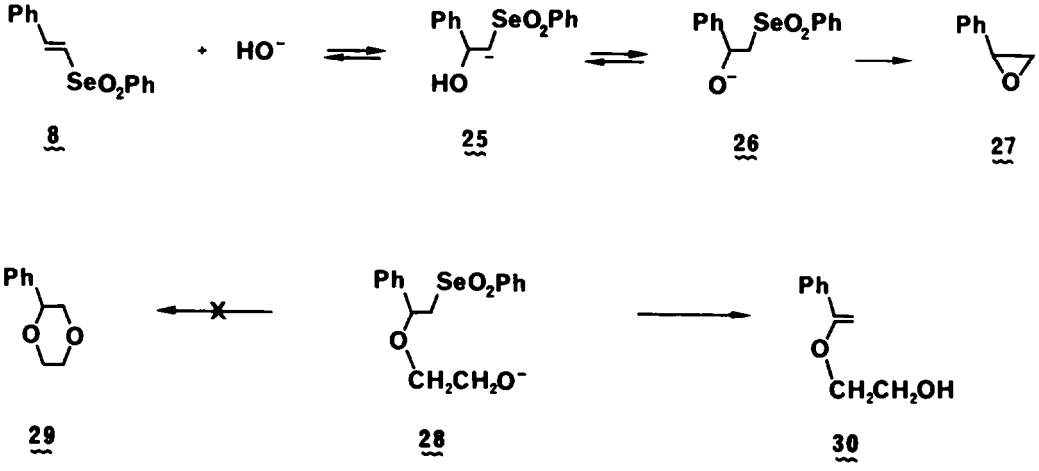
9 13 8

23 : Nu = MeS
24 : Nu = MeO

interpretation is corroborated by the fact that when **9a** is treated with an insufficient quantity of MeONa compound **8** can be isolated from the reaction mixture which contains unreacted **9a** together with some **20** and **24**. It is interesting to note that compounds **20** and **24** were also obtained from the reactions of **8** with MeONa in DMF. The present results thus support the interpretation of the behaviour of vinyl selenones towards alkoxides in DMF given in the previous work.[1] Thus, the results collected in Scheme 6 show that in DMF the MeS anion attacks the α-carbon and the α-hydrogen of compounds **9**, whereas the MeO anion attacks the α- and the β-hydrogens; the abstraction of the α-hydrogen which initiates the retro Michael process is very likely occurring in methanol also but in this case the carbanion **13** can easily revert to **9** which is consumed by the other irreversible processes (Scheme 5).

Experiments were also carried out to effect the addition of hydroxide ions to the vinyl selenone **8**; the reactions were carried out with potassium hydroxide in water using tetrahydrofuran as a cosolvent. The reaction in this case does not stop at the stage of the conjugate addition product but it proceeds further to afford the epoxide **27**, although in low yields (45%). The formation of **27** can be explained (Scheme 8) assuming that the initially formed carbanion **25** gives the β-hydroxyselenone from which the alkoxy anion **26** is produced; intramolecular nucleophilic displacement affords **27**. Anions like **26** are very likely responsable for the observed formation of epoxides from the reaction of aryl alkyl selenones with potassium t-butoxide in THF in the presence of belzaldehyde.[10] It has been shown by Kuwajima and coworkers[6,8] that alkoxide ions derived from hydroxyselenones give a similar intramolecular displacement to afford oxethanes. On the contrary, the anion **28**, produced from **9e** with NaH in THF, did not give any phenyl dioxane **29**,

SCHEME 8



the only isolated reaction product being the alkene **30** (82%). As suggested above alkoxy anions behave as bases rather than as nucleophiles and in the case of the anion **28** the intramolecular elimination reaction is greatly favoured by a six membered transition state.

The results discussed in the present and in the previous[1] paper indicate that the reactivity of vinyl selenoxides and vinyl selenones with oxygen and sulphur nucleophiles changes on passing from dipolar aprotic to protic solvents; similar changes in reactivity are also produced in the case of aryl alkyl selenones. Thus vinyl selenoxides, vinyl selenones and their conjugate addition products are very versatile intermediates which can be easily transformed into a series of

valuable compounds. All these reactions are made possible by the peculiar properties of the seleninyl and the selenonyl groups which are strong electron-attracting substituents. In particular, the ArSeO group acts as good leaving group in nucleophilic vinylic substitutions when the reactions are carried out in dipolar aprotic solvents. The $ArSeO_2$ group shows several interesting characteristics; it activates the carbon-carbon double bond towards the addition of anionic reagents and at same time it acts as a good leaving group in nucleophilic substitutions (both aliphatic and vinylic) and in elimination reactions. Moreover the α-hydrogen atoms in aryl alkyl selenones have acidic properties. Thus, as anticipated in the introduction, the appropriate choice of the reagent and of the reaction solvent allows to direct the reactions of vinyl selenoxides, vinyl selenones and their conjugate addition products towards the desired derivatives with loss of the selenium containing functions.

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; carbon-13 nmr spectra were recorded at 20.15 MHz on a Bruker WP 80 SY instrument operating in the Fourier transform mode with proton decoupling throughout. In some cases assignments were made by off-resonance experiments. $CDCl_3$ was used as solvent and TMS as reference. Elemental analyses were carried out on a Carlo Erba Model 1106 Elemental Analizer. Glc analyses were performed on a Hewlett-Packard 5830 A chromatograph with a 20 in. 10% UCW 982 column.

Compounds **5**, **8**, **10**, and **11** were prepared as described in the previous paper.[1] (E)-β-Styryl phenyl selenide **7**, α-methoxystyrene **20**, (E)-β-styryl methyl sulphide **23** and (E)-β-methoxystyrene **24** have already been described.

Reactions of the (E)-β-styryl phenyl selenone 8 with alkoxides.

To the selenone **8** (5 mmol), dissolved in methanol or in ethanol (15 ml) and cooled in an ice bath, sodium methoxide or ethoxide (5 mmol) was added under stirring. In the other cases a solution of the alkoxide in the alcohol was prepared by adding sodium hydride (5 mmol) to the alcohol and the selenone **8** was then added. The progress of the reaction was monitored by glc. The reaction times were as follows: **9a**, 2 h; **9b**, 4 h; **9c**, 2.5 h; **9d**, 4.5 h; **9e**, 12 h. The reaction mixtures containing the insoluble white products **9** were poured on water and extracted with chloroform. After washing with water the chloroform was dried and evaporated. The solid residue was purified by washing with light petroleum. Further purification can be effected by dissolving the solid in ethanol at room temperature and cooling the resulting solution in an ice bath. Compound **9a** was similarly prepared starting from **10**. The reaction of the (E)-β-styryl methyl selenone **11** with MeONa in MeOH was carried out in a similar way. Reaction yields are given under the Results and Discussion section (Scheme 2); physical, spectral and analytical data are reported below.

1-Phenyl,1-methoxy,2-phenylselenonylethane, **9a**, m.p. 171-3°C. ^{1}H-nmr δ 8.1 - 7.9 (m, 2 H), 7.7 - 7.5 (m, 3 H), 7.3br (s, 5 H), 4.95 (dd, 1 H, J = 10.8 and 3.0 Hz), 3.9 (dd, 1 H, J = 12.5 and 10.8 Hz), 3.6 (dd, 1 H, J = 12.5 and 3.0 Hz), 3.15 (s, 3 H). ^{13}C-nmr δ 143.9, 137.2, 133.9, 129.8, 129.1, 127.1, 126.6, 77.2 (C-1), 66.8 (C-2), 56.6 (Me). Anal. Calcd for $C_{15}H_{16}O_3Se$: C, 55.73; H, 5.00. Found: C, 55.81; H, 4.97.

1-Phenyl,1-ethoxy,2-phenylselenonylethane, **9b**, m.p. 136-8°C. ^{1}H-nmr δ 8.15 - 7.95 (m, 2 H), 7.7 - 7.55 (m, 3 H), 7.3br (s, 5 H), 5.05 (dd, 1 H, J = 10.8 and 3.0 Hz), 3.9 (dd, 1 H, J = 12.5 and 10.8 Hz), 3.6 (dd, 1 H, J = 12.5 and 3.0 Hz), 3.3 (q, 2 H, J = 7.2 Hz), 0.95 (t, 3 H, J = 7.2 Hz). ^{13}C-nmr δ 133.8, 129.8, 129.1, 129.0, 127.2, 126.5, 75.4 (C-1), 66.7 (C-2), 64.6 (CH_2), 14.7 (Me). Anal. Calcd for $C_{16}H_{18}O_3Se$: C, 56.97; H, 5.39. Found: C, 57.02; H, 5.33.

1-Phenyl,1-isopropoxy,2-phenylselenonylethane, **9c**, m.p. 145-7°C. ^{1}H-nmr δ 8.1 - 7.95 (m, 2 H), 7.7 - 7.5 (m, 3 H), 7.3br (s, 5H), 5.2 (dd, 1 H, J = 10.5 and 2.7 Hz), 3.95 (dd, 1 H, J = 12.5 and 10.5 Hz), 3.6 (dd, 1 H, J = 12.5 and 2.7 Hz), 3.5 (spt, 1 H, J = 6 Hz), 1.1 (d, 3 H, J = 6.0 Hz), 0.85 (d, 3 H, J = 6.0 Hz). ^{13}C-nmr δ 144.2, 138.5, 133.7, 129.7, 129.0, 128.9, 127.1, 126.6, 72.5 (C-1), 69.7 (CH), 66.6 (C-2), 22.9 (Me), 20.6 (Me). Anal. Calcd for $C_{17}H_{20}O_3Se$: C, 58.11; H, 5.75. Found: C, 58.00; H, 5.74.

1-Phenyl,1-allyloxy,2-phenylselenonylethane, **9d**, m.p. 107-8°C. ^{1}H-nmr δ 8.1 - 7.95 (m, 2 H), 7.65 - 7.5 (m, 3 H), 7.3br (s, 5 H), 5.65 (ddt, 1 H, J = 18.0, 9.0 and 5.4 Hz), 5.15 - 4.9 (m, 2 H), 5.1 (dd, 1 H, J = 10.5 and 3.0 Hz), 3.95 (dd, 1 H, J = 12.5 and 10.5 Hz), 3.8 (dt, 2 H, J = 5.4 and 1.2 Hz), 3.65 (dd, 1 H, J = 12.5 and 3.0 Hz). ^{13}C-nmr δ 143.9, 137.4, 133.8, 133.5 (vin-C), 129.9, 129.2, 127.3, 126.7, 117.5 (vin-C), 75.0 (C-1), 69.9 (CH_2), 66.7 (C-2). Anal. Calcd for $C_{17}H_{18}O_3Se$: C, 58.45; H, 5.20. Found: C, 58.51; H, 5.23.

1-Phenyl,1-(2-hydroxy)ethoxy,2-phenylselenonylethane, **9e**, m.p. 118-20°C. ^{1}H-nmr δ 8.15 - 7.95 (m, 2 H), 7.7 - 7.5 (m, 3 H), 7.35br (s, 5 H), 5.25 (dd, 1 H, J = 10.8 and 3.0 Hz), 4.0 (dd, 1 H, J = 12.5 and 10.8 Hz), 3.75 (dd, 1 H, J = 12.5 and 3.0 Hz), 3.7 - 3.3 (m, 5 H). ^{13}C-nmr δ 134.2, 130.2, 129.2, 127.0, 126.6, 74.9 (C-1), 70.5 (CH_2), 66.8 (C-2), 60.6 (CH_2). Anal. Calcd for $C_{16}H_{18}O_4Se$: C, 54.39; H, 5.14. Found: C, 54.42; H, 5.12.

1-Phenyl,1-methoxy,2-methylselenonylethane, **12**, m.p. 127-9°C. ^{1}H-nmr δ 7.35br (s, 5 H), 4.9 (dd, 1 H, J = 10.8 and 3.0 Hz), 3.8 (dd, 1 H, J = 12.5 and 10.8 Hz), 3.45 (dd, 1 H, J = 12.5 and 3.0 Hz), 3.3 (s, 3 H), 3.25 (s, 3 H). ^{13}C-nmr δ 137.0, 129.2, 126.7, 77.3 (C-1), 65.0 (C-2), 56.7 (OMe), 45.7 (Me). Anal. Calcd for $C_{10}H_{14}O_3Se$: C, 45.98; H, 5.41. Found: C, 46.00; H, 5.43.

Reactions of the (E)-β-styryl phenyl selenone 8 with MeSNa in MeOH.

To a solution of **8** (5 mmol) in MeOH (15 ml), cooled in an ice bath, solid MeSNa (10 mmol) was added. The starting selenone was consumed in 1 h. The reaction was worked up as described above and the residue was chromatographed on a silica gel column using a mixture of light petroleum and ether (97:3) as eluant. Reaction products and reaction yields are given under the Results and Discussion section (Scheme 4); physical, spectral and analytical data of the isolated products are given below. Under the same conditions the reaction of **8** (5 mmol) with excess MeSNa (50 mmol) afforded compound **14** only.

1,2-Bis(methylthio)phenylethane, **14**, oil. ^{1}H-nmr δ 7.4 - 7.1 (m, 5 H), 3.85 (dd, 1 H, J = 8.5 and 6.5 Hz), 3.1 - 2.9 (m, 2 H), 1.95 (s, 3 H), 1.9 (s, 3 H). ^{13}C-nmr δ 128.4, 127.9, 127.4, 51.5 (C-1), 40.3 (C-2), 16.3 (Me), 14.6 (Me). Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.55; H, 7.13. Found: C, 60.47; H, 7.16.

1-Phenyl,1-methoxy,2-methylthioethane, **15a**, oil. ^{1}H-nmr δ 7.35br (s, 5 H), 4.4 (dd, 1 H, J = 7.5 and 5.7 Hz), 3.25 (s, 3 H), 2.9 (dd, 1 H, J = 13.2 and 7.5 Hz), 2.65 (dd, 1 H, J = 13.2 and 5.7 Hz), 2.05 (s, 3 H). ^{13}C-nmr δ 140.8, 128.3, 127.8, 126.6, 83.9 (C-1), 56.7 (OMe), 41.8 (C-2), 16.5 (SMe). Anal. Calcd for $C_{10}H_{14}OS$: C, 65.88; H, 7.76. Found: C, 65.79; H, 7.68.

Reactions of the β-alkoxyalkyl phenyl selenones 9 with MeSNa or MeONa in MeOH.

To a solution of **9** (5 mmol), in methanol (15 ml), MeSNa (10 mmol) or MeONa (20 mmol) was added. The mixture was stirred at room temperature until the starting selenone was consumed (tlc); reaction times were 2 - 6 h in the case of MeSNa and 8 - 10 h in the case of MeONa. The mixture was poured on water, extracted with chloroform, worked up in the usual way and chromatographed through a silica gel column using mixtures of light petroleum and ether (from 97:3 to 90:10) as eluant. Under these conditions the α-alkoxystyrenes are partially converted into acetophenone. The reaction mixtures deriving from the reactions with MeONa were therefore chromatographed through a deactivated alumina column. Reaction products and reaction yields are given under the Results and Discussion section (Scheme 5); physical, spectral and analytical data of the isolated products are reported below. Compounds **15a** and **20** have already been described.

1-Phenyl,1-ethoxy,2-methylthioethane, **15b**, oil. ^{1}H-nmr δ 7.35br (s, 5 H), 4.4 (dd, 1 H, J = 7.5 and 5.7 Hz), 3.35 (q, 2 H, J = 7.0 Hz), 2.9 (dd, 1 H, J = 13.2 and 7.5 Hz), 2.65 (dd, 1 H, J = 13.2 and 5.7 Hz), 2.1 (s, 3 H), 1.2 (t, 3 H, J = 7.0 Hz). ^{13}C-nmr δ 141.7, 128.4, 127.9, 126.7, 82.3 (C-1), 64.5 (CH_2), 42.1 (C-2), 16.7 (SMe), 15.3 (Me). Anal. Calcd for $C_{11}H_{16}OS$: C, 67.29; H, 8.23. Found: C, 67.33; H, 8.26.

1-Phenyl,1-(2-hydroxy)ethoxy,2-methylthioethane, **15e**, oil. ^{1}H-nmr δ 7.3br (s, 5 H), 4.4 (dd, 1 H, J = 8.1 and 5.1 Hz), 3.8 - 3.55 (m, 2 H), 3.55 - 3.35 (m, 2 H), 2.9 (dd, 1 H, J = 13.8 and 8.1 Hz), 2.75br (s, 1 H), 2.65 (dd, 1 H, J = 13.8 and 5.1 Hz), 2.1 (s, 3 H). ^{13}C-nmr δ 128.5, 127.9, 126.4, 82.0 (C-1), 70.3 (CH_2), 61.7 (CH_2), 42.1 (C-2), 16.4 (Me). Anal. Calcd for $C_{11}H_{16}O_2S$: C, 62.22; H, 7.61. Found: C, 62.26; H, 7.58.

1-Phenyl,1-methoxy,2-phenylselenoethane, **18a**, oil (Lit.[14] b.p. 181-2°C/8 mm). ^{1}H-nmr δ 7.55 - 7.35 (m, 2 H), 7.3br (s, 5 H), 7.25 - 7.1 (m, 3 H), 4.35 (dd, 1 H, J = 7.8 and 5.4 Hz), 3.4 (dd, 1 H, J = 12.0 and 7.8 Hz), 3.25 (s, 3 H), 3.1 (dd, 1 H, J = 12.0 and 5.4 Hz). ^{13}C-nmr δ 132.6, 129.0, 128.6, 128.1, 126.8, 126.7, 83.3 (C-1), 57.0 (Me), 35.4 (C-2). The proton nmr data correspond to those reported in the literature.[14]

1-Phenyl,1-ethoxy,2-phenylselenoethane, **18b**, oil. ^{1}H-nmr δ 7.55 - 7.4 (m, 2 H), 7.25br (s, 5 H), 7.2 - 7.0 (m, 3 H), 4.45 (dd, 1 H, J = 8.1 and 5.4 Hz), 3.4 (q, 2 H, J = 7.2 Hz), 3.35 (dd, 1 H, J = 12.3 and 8.1 Hz), 3.05 (dd, 1 H, J = 12.3 and 5.4 Hz), 1.15 (t, 3 H, J = 7.2 Hz). ^{13}C-nmr δ 141.7, 132.6, 129.0, 128.5, 128.0, 126.8, 126.7, 81.6 (C-1), 64.7 (CH_2), 35.7 (C-2), 15.3 (Me). Anal. Calcd for $C_{16}H_{18}OSe$: C, 62.94; H, 5.95. Found: C, 62.87; H, 5.98. This product is identical to an authentic sample prepared independently.[12]

1-Phenyl,1-(2-hydroxy)ethoxy,2-phenylselenoethane, **18e**, oil. ^{1}H-nmr δ 7.5 - 7.3 (m, 2 H), 7.25 - 7.0 (m, 8 H), 4.4 (dd, 1 H, J = 8.7 and 4.8 Hz), 3.7 - 3.3 (m, 4 H), 3.25 (dd, 1 H, J = 12.6 and 8.7 Hz), 3.05 (dd, 1 H, J = 12.6 and 4.8 Hz), 2.5br (s, 1 H). ^{13}C-nmr δ 141.0, 132.6, 129.0, 128.5, 128.0, 126.9, 126.4, 81.8 (C-1), 70.4 (CH_2), 61.6 (CH_2), 35.7 (C-2). Anal. Calcd for $C_{16}H_{18}O_2Se$: C, 59.81; H, 5.66. Found: C, 59.77; H, 5.70.

1,2-Bis(methoxy)phenylethane, **19**, oil. ^{1}H-nmr δ 7.3br (s, 5 H), 4.4 (dd, 1 H, J = 7.8 and 4.2 Hz), 3.8 - 3.2 (m, 2 H), 3.4 (s, 3 H), 3.3 (s, 3 H). ^{13}C-nmr δ 139.0, 128.4, 127.9, 126.9, 83.0 (C-1), 77.3 (C-2), 59.1 (Me), 56.9 (Me). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.24; H, 8.51. Found: C, 72.30; H, 8.55.

1,2-Bis(ethoxy)phenylethane, **21**, oil. ^{1}H-nmr δ 7.3br (s, 5 H), 4.45 (dd, 1 H, J = 7.5 and 4.5 Hz), 3.75 - 3.25 (m, 6 H), 1.2 (t, 6 H, J = 7.2 Hz). ^{13}C-nmr δ 140.3, 128.3, 127.7, 126.9, 81.5 (C-1), 75.5 (C-2), 66.8 (CH_2), 64.5 (CH_2), 15.4 (Me), 15.1 (Me). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.17; H, 9.36. Found: C, 74.10; H, 9.25.[15]

α-Ethoxystyrene, **22**, oil (Lit.[15] b.p. 109-112°C/30 mm). ^{1}H-nmr δ 7.7 - 7.5 (m, 2 H), 7.35 - 7.15 (m, 3 H), 4.6 (d, 1 H, J = 2.5 Hz), 4.2 (d, 1 H, J = 2.5 Hz), 3.9 (q, 2 H, J = 7.2 Hz), 1.4 (t, 3 H, J = 7.2 Hz). ^{13}C-nmr δ 160.1 (vin-C), 136.8 (ipso-C), 128.4, 128.1, 125.5, 82.2 (vin-C), 63.3 (CH_2), 14.5 (Me). The proton[16] and carbon-13[17] nmr data correspond to those reported in the literature.

Reactions of the β-alkoxyalkyl phenyl selenones 9 with MeSNa or MeONa in DMF.

To a solution of **9** (5 mmol), in DMF (15 ml), cooled at 0°C in an ice bath, MeSNa (6 mmol) or MeONa (10 mmol) was added under stirring. The reactions were complete after 0.5 h and were worked up in the usual way. The product isolated by column chromatography (on silica gel or on alumina in the case of the reactions with MeSNa or MeONa, respectively) and the reaction yields are given under the Results and Discussion section (Scheme 6). Compounds **15a**, **15e**, **20**, **23**, and **24** have already been described. The data of compound **15d** are reported below.

1-Phenyl,1-allyloxy,2-methylthioethane, **15d**, oil. ^{1}H-nmr δ 7.35br (s, 5 H), 5.85 (ddt, 1 H, J = 18.0, 10.2 and 5.4 Hz), 5.2 (ddt, 1 H, J = 18.0, 2.4 and 1.5 Hz), 5.1 (ddt, 1 H, J = 10.2, 2.4 and 1.2 Hz), 4.45 (dd, 1 H, J = 7.2 and 5.7 Hz), 3.9 (ddd, 2 H, J = 5.4, 1.5 and 1.2 Hz), 2.9 (dd, 1 H, J = 13.2 and 7.2 Hz), 2.65 (dd, 1 H, J = 13.2 and 5.7 Hz), 2.05 (s, 3 H). ^{13}C-nmr δ 141.2, 134.8 (vin-C), 128.4, 127.9, 126.8, 116.7 (vin-C), 81.6 (C-1), 69.7 (CH_2), 41.9 (C-2), 16.7 (Me). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.17; H, 7.76. Found: C, 69.23; H, 7.80.

Reaction of the (E)-β-styryl phenyl selenone 8 with KOH in THF.

The selenone **8** (5 mmol) was added to a solution of KOH (7.5 mmol) in water (7 ml) and THF (3 ml) and the mixture was stirred at 50°C for 18 h. The mixture was poured on water and extracted with chloroform. After the usual work up the residue was chromatographed through a silica gel column using chloroform as eluant. The phenylethylene oxide **27** was obtained in 45% yields. Glc retention time and proton nmr spectrum were identical to those of the commercial product.

Reaction of 1-phenyl,1-(2-hydroxy)ethoxy,2-phenylselenonylethane 9e with NaH in THF.

Sodium hydride (5 mmol) was added to a solution of **9e** (5 mmol) in THF (15 ml) and the mixture was stirred at room temperature for 10 h. After the usual work up the reaction product was purified by column chromatography on deactivated alumina using a mixture of light petroleum and ether (95:5) as eluant. Compound **30** was obtained in 82% yields.

α-(2-Hydroxy)ethoxystyrene, **30**, oil. ^{1}H-nmr δ 7.65 - 7.45 (m, 2 H), 7.3 - 7.15 (m, 3 H), 4.65 (d, 1 H, J = 2.5 Hz), 4.2 (d, 1 H, J = 2.5 Hz), 3.9br (s, 4 H), 2.4br (s, 1 H). ^{13}C-nmr δ 159.8 (vin-C), 136.3 (ipso-C), 128.5, 128.1, 125.4, 83.0 (vin-C), 69.1 (CH_2), 61.2 (CH_2). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.13; H, 7.38. Found: C, 73.18; H, 7.35.

Acknowledgments. We gratefully acknowledge financial support from the CNR, Rome and Ministero della Pubblica Istruzione, Italy.

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