Tetrahedron Vol. 44, No. 8, pp. 2273 to 2282, 1988
Printed in Great Britain.

0040–4020/88 $3.00 + .00

SELENIUM CATALYZED CONVERSION OF VINYL HALIDES INTO α-ALKOXY ACETALS

Marcello Tiecco,* Lorenzo Testaferri,* Marco Tingoli, Donatella Chianelli and Donatella Bartoli

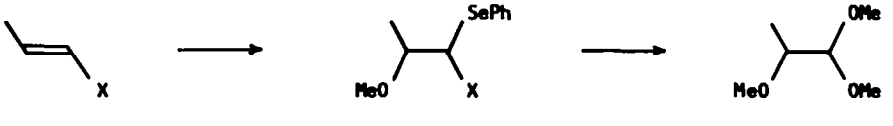
Istituto di Chimica Organica, Facoltà di Farmacia, Università di Perugia, Italy.

(*Received in UK* 18 *January* 1988)

Abstract: The reaction of vinyl halides with phenylselenenyl chloride in alcohols affords α-alkoxy acetals and diphenyl diselenide which can be oxidized to PhSe cations by nitrate or persulfate anions. The reaction can be carried out with catalytic amounts of PhSeCl or PhSeSePh. The reaction proceeds through the formation of the methoxyselenenylation product which then suffers solvolysis. Under controlled conditions, the 1-phenyl-1-methoxy-2-bromo-2-phenylselenenyl ethane was isolated from the reaction of β-bromostyrene and PhSeCl in methanol. Several deselenenylation reactions of this α-halogenoselenide are reported.

We have recently observed that the reaction with excess phenylselenenyl chloride in methanol represents a convenient procedure to effect the one-pot methoxyselenenylation-deselenenylation of alkenes.[1] Thus, α- and β-alkyl or aryl styrenes reacted with PhSeCl in MeOH to give α-methoxy phenylselenenyl alkanes, $PhCR(OMe)CHR_1SePh$, which were transformed into chloromethoxy alkanes, $PhCR(OMe)CHR_1Cl$, and/or dimethoxy alkanes, $PhCR(OMe)CHR_1(OMe)$; with β-substituted styrenes phenyl migration also occurred to afford acetals, $PhCRR_1CH(OMe)_2$. These reactions also apply to alkenes having more complex structures.[2]

We now report the results of a related investigation carried out on vinyl halides. The reaction of vinyl halides with PhSeCl in MeOH affords β-methoxy, α-halogenoselenides 1 which are rapidly transformed into α-methoxy acetals 2 and diphenyl diselenide. In the presence of a suitable oxidant PhSe cations can be regenerated and the reaction can therefore be effected with catalytic amounts of PhSeCl or PhSeSePh.



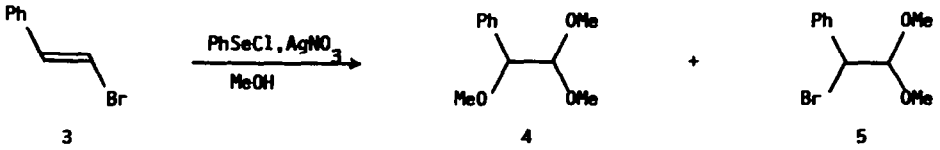
1 2

α-Halogenoselenides **1** represent an interesting class of compounds in which the juxtaposition of halogen and selenium atoms attached to the same carbon atom can give rise to several useful conversions. The chemistry of the corresponding sulfur compounds is well documented; α-chlorosulfides are useful as aldehyde or ketone equivalents, as reactive electrophiles for a variety of sulfur-mediated reactions and as precursors of α-chlorosulfones.[3] α-Halogenoselenides can be expected to present a similar behaviour; moreover they can also give rise to other reactions which are peculiar of the selenium derivatives. Few reports on the synthesis and on the reactivity of α-halogenoselenides can be found in the literature.[4-9] Some reactions of these compounds are reported in the present paper.

RESULTS AND DISCUSSION

Most of the experiments described below were carried out on (E)-β-bromostyrene. Some reactions were also carried out on the (E)-β-methoxy- and (E)-β-phenylselenenyl styrenes. Other vinyl halides investigated were the bromostilbene and the 1-bromo-1-octene.

The reaction of (E)-β-bromostyrene **3** with PhSeCl in MeOH does not give any reaction product, not even in the presence of triethylamine; this indicates that the substrate is less reactive than the α- or β-alkyl or aryl styrenes which under these conditions easily give rise to the methoxyselenenylation products.[1,10] However, when silver nitrate (1 molar equivalent) was added the reaction was complete after 2 h at room temperature. From the resulting strongly acid and brown solution, together with diphenyl diselenide two other compounds were isolated; these were identified as the 1-phenyl-1,2,2-trimethoxy ethane **4** (90%) and the 1-phenyl-1-bromo-2,2-dimethoxy ethane **5** (5%):

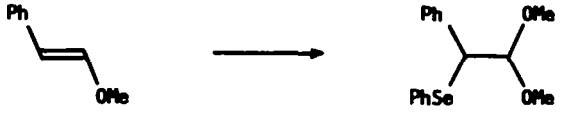


3 **4** **5**

The brown color of the final reaction mixture was indicative of the presence of the PhSe cation and in fact, if styrene was added, the mixture became almost colorless and after work up, together with **4** and **5**, the addition product $PhCH(OMe)CH_2SePh$ was isolated in 80% yield. Thus in the presence of $AgNO_3$ a complete conversion of **3** into **4** and **5** was obtained and the $PhSe^+$ employed was almost completely recovered. Silver sulphate was also capable of effecting the same conversion, compounds **4** and **5** being obtained in yields similar to those observed with $AgNO_3$. In this case however PhSe cations were not present in the final reaction mixture and the selenium employed was recovered as PhSeSePh; treatment with styrene did not give the addition product $PhCH(OMe)CH_2SePh$. These results indicate that an important role is played by the nitrate ions. As a matter of fact, a reaction carried out with KNO_3 gave results identical to those observed with $AgNO_3$. The reaction mixture contained **4**, **5**, and PhSe cations; moreover nitrite ions were detected in the aqueous phase. It can be therefore suggested that the reaction of **3** with PhSeCl affords **4**, **5** and PhSeSePh and that, in the presence of nitrate ions, this latter compound is oxidized to $PhSe^+$. Two important consequences emerge from these results. The use of nitrate ions should allow to effect the reaction also starting from PhSeSePh and moreover the conversion of **3** should proceed also using a catalytic amount of the PhSe cation precursor. This has been verified experimentally. Thus, compounds **4** (82%) and **5** (5%) were easily produced when **3** (4 mmol) was allowed to react with

KNO_3 (4 mmol), PhSeSePh (2 mmol) and few drops of HNO_3 in methanol at room temperature for 3 h; PhSe cations were also present in the final reaction mixture. On the other hand, the reaction of **3** (5 mmol) with KNO_3 (5 mmol) and PhSeCl (0.5 mmol), in methanol at room temperature for 6 h (or at 60 °C for 3 h), afforded **4** and **5** in 92 and 4.5% yields respectively.

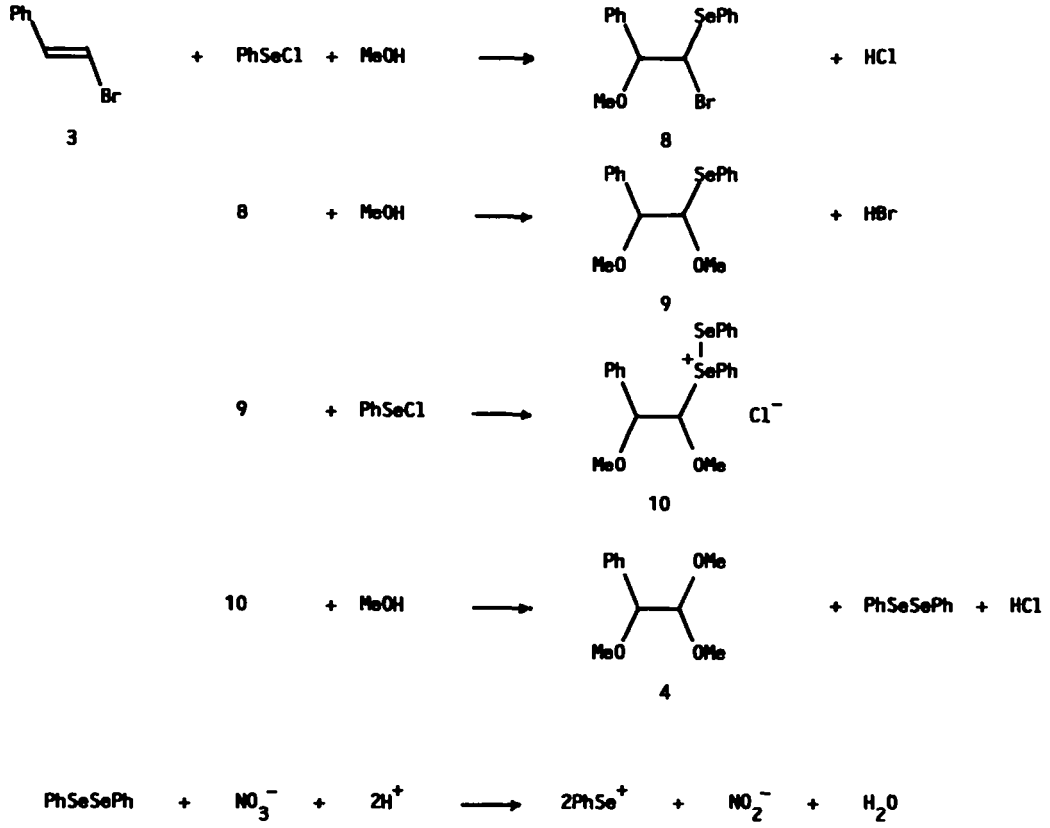
Independent experiments showed that **5** is not a precursor of **4** since it was recovered unchanged when it was treated with PhSeCl in MeOH in the presence of KNO_3. Similarly, 1-phenyl-1-phenylselenenyl-2,2-dimethoxy ethane **7**, which was obtained from β-methoxystyrene **6** (in 87% yield) by reaction with PhSeCl and KNO_3 in methanol seems not to be involved in the reaction of **3**, since it was recovered unchanged when allowed to react with PhSeCl under the same conditions.



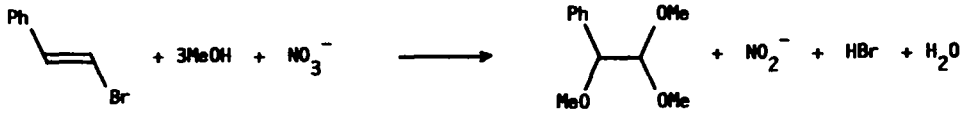
6 **7**

On the basis of these observations the conversion of β-bromostyrene into the α-methoxy acetal **4** can be suggested to proceed as indicated in Scheme 1. The regiospecific addition (see below) of PhSeCl to **3** affords the α-bromoselenide **8** which rapidly solvolyzes (through a selenium stabilyzed carbocation) to give the 1-phenyl-1,2-dimethoxy-2-phenylselenenyl ethane **9**; this suffers attack by PhSeCl to give a selenonium chloride intermediate **10** from which the final product **4** and PhSeSePh are obtained. The nitrate ions then oxidize the diphenyl diselenide to PhSe cations.

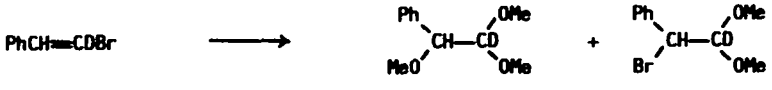
SCHEME 1



Addition of the five equations reported in Scheme 1 leads to the following global reaction which indicates that PhSeCl or PhSeSePh are only involved as catalysts:



The proposed mecchanism is further supported by the results of independent experiments from which some of the proposed intermediates could be isolated and studied. The 1-phenyl-1-methoxy-2-bromo-2-phenylselenenyl ethane **8** could be isolated in 70% yield when **3** was allowed to react with an insufficient quantity of PhSeCl (0.5 molar equivalents) at -10 °C for 6 - 8 h. Compound **8** was obtained as a single diastereoisomer (erythro) indicating that the methoxy-selenenylation of **3** is a stereospecific process. By treatment with PhSeCl in MeOH at room temperature, **8** was quantitatively converted into **4**. On the contrary, if **8** was simply dissolved in methanol, compound **9** was obtained; minute amounts of 1-phenyl-1,2-dimethoxy-2-bromo ethane **11** were also obtained. The selenide **9** was stable in methanol; however, if PhSeCl was added, it quantitatively gave the acetal **4**. In the previously studied PhSeCl promoted displacement of the phenylselenenyl group on the selenides PhCH(OMe)CHRSePh (R = Me, CH_2Ph, Ph)[1] it was shown that selenonium chlorides of the type $PhCH(OMe)CHRSeClPh^+ Cl^-$ were involved as intermediates.[11] It was also observed that the substitution of the PhSe by the MeO group was accompanied by the 1,2-shift of the phenyl group to give the acetals $PhCHRCH(OMe)_2$. In the present case the structure of the reaction product **4** does not give any information about this problem. For this purpose an experiment was carried out using the deuterated bromostyrene **12**; this experiment was also important to understand how the by-product **5** originates. From the reaction of **12** with PhSeCl in MeOH compounds **13** and **14** were isolated with yields similar to those observed in the reaction of **3**.

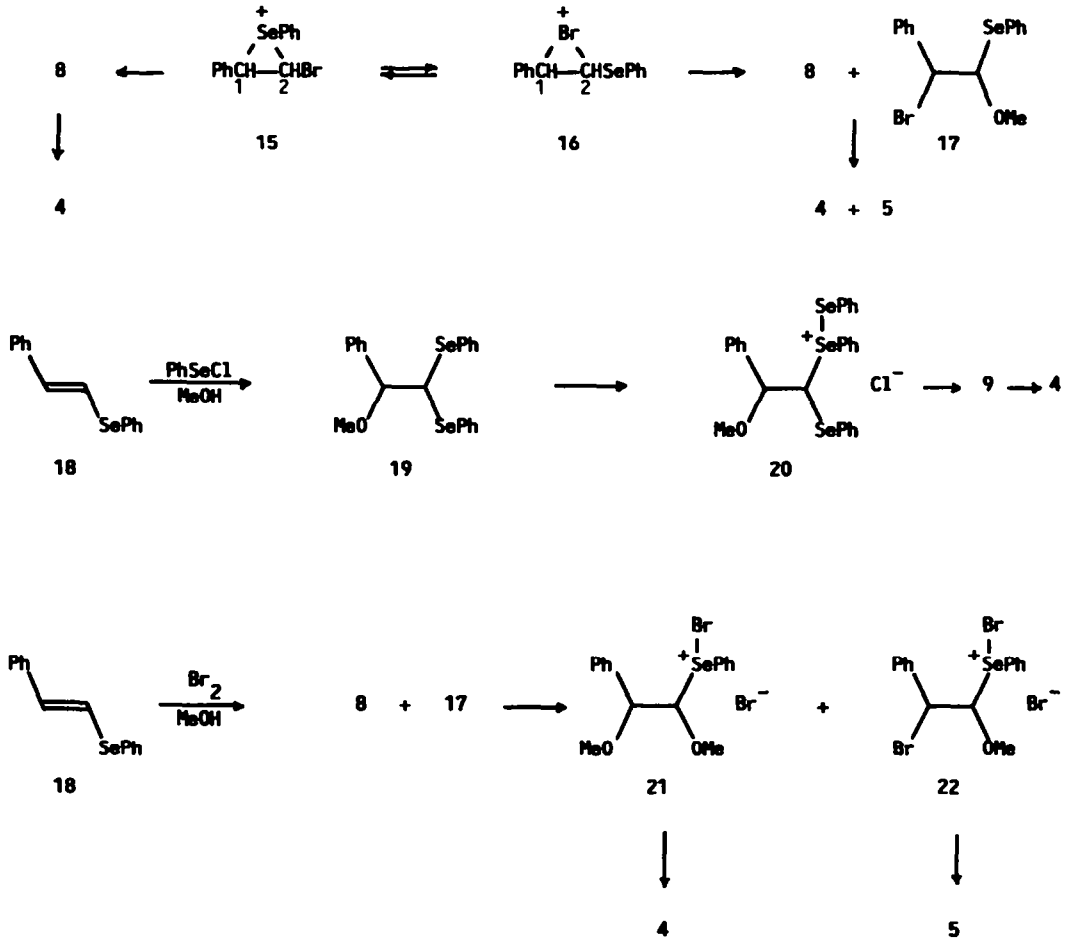


12 **13** **14**

The formation of **13** indicates that phenyl migration does not occur during the conversion of **3** into the acetal **4**. Very likely the ionization of the carbon-selenium bond in the selenonium chloride **10** does not require the assistance of the vicinal phenyl group since the resulting carbocation is stabilized by the methoxy group. Morever, the formation of **14** indicates that **5** does not form by phenyl migration (which could occur during the solvolysis of **8**) but rather by bromine migration. This could be explained assuming that the seleniranium cation **15**, which is the first intermediate[12] which forms from the interaction of **3** with PhSeCl, partially isomerizes to the bromonium ion **16** (Scheme 2). From **15** the only product obtained is **8**, which derives from the attack of methanol on carbon-1. On the contrary, in the case of **16** attack at carbon-1 would afford **8**, whereas attack at carbon-2 would give **17** which is rapidly transformed into **5** by reaction with $PhSe^+$ (Scheme 2).[13] This interpretation implies that the reaction of the seleniranium cations, like **15**, is regiospecific, whereas that of the bromonium ions, like **16**, is not regiospecific. This

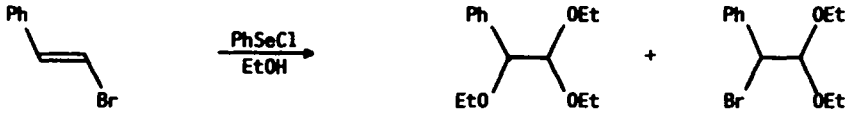
has been tested by means of some independent experiments. The reaction of β-phenylselenenyl styrene **18** with PhSeCl in methanol in the presence of KNO_3 afforded **4** as the sole reaction product (82% yield).

SCHEME 2



When the same substrate **18** was treated with bromine (in methanol and with KNO_3) a mixture of **4** (60%) and **5** (30%) was instead obtained. Thus, the reaction of **18** with PhSeCl, which involves a seleniranium cation intermediate similar to **15**, is regiospecific and it can be suggested to afford **4** through the intermediate formation of the α-bisselenide **19**, the selenonium chloride **20** and the selenide **9**. On the contrary, the reaction of **18** with bromine, which should involve the bromonium ion **16**, is not regiospecific. The final products very likely originate from the addition products **8** and **17**, in this case the ionization of the carbon selenium bond (at least at first stages of the reaction when $PhSe^+$ cations are not yet present in the reaction mixture) should occur on the selenonium bromides **21** and **22**.

The reaction of **3** with PhSeCl and KNO_3 could also be carried out in ethanol. In this case however the reaction was slower than in methanol[14] and it was complete only after 2 h at 60 °C. 1-Phenyl-1,2,2-triethoxy ethane **23** (78%) and 1-phenyl-1-bromo-2,2-diethoxy ethane **24** (10%) were obtained.



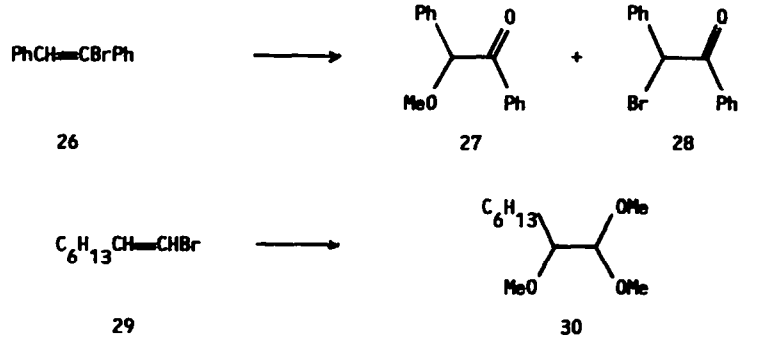
3 23 24

The oxidation pf PhSeSePh to $PhSe^+$ can be effected with oxidizing agents different from the nitrate ions. For this purpose persulphate ions were very efficient:[15]

The reaction of **3** (5 mmol) with diphenyl diselenide (2.5 mmol) and $(NH_4)_2S_2O_8$ (10 mmol) in methanol was complete after 15 min at reflux and afforded **4** in 95% yield; PhSe cations were also present as indicated by the formation of $PhCH(OMe)CH_2SePh$ (90%) after addition of styrene to the final reaction mixture. This procedure however cannot be applied when PhSeSePh is used in catalytic amounts since the $S_2O_8^{--}$ oxidizes the bromide ions to bromine and this also adds to ß-bromostyrene. Thus, under these conditions three products were formed in comparable amounts, i.e. **4**, **5** and the 1-phenyl-1-methoxy-2,2-dibromo ethane **25**.

Other vinyl bromides were then investigated. The reaction of bromostilbene **26** (3 mmol) with PhSeSePh (1.5 mmol) and $(NH_4)_2S_2O_8$ (6 mmol) in MeOH, at reflux for 3 h, afforded the 2-methoxy-2-phenyl acetophenone **27** (40%) and the 2-bromo-2-phenyl acetophenone **28** (45%), which very likely derive from the expected dimethyl ketals which suffered deprotection during the work up (Scheme 3). The formation of the bromo derivative as the major reaction product is noteworthy. Under the reasonable assumption that the mecchanism of formation of **28** is similar to that proposed in Scheme 2 for the formation of **5**, this result suggests that bromine migration is now much more important than in the reaction of **3**; very likely the presence of the phenyl group stabilizes the bromonium ion or the carbocation $PhCHBr\overset{+}{C}PhSePh$ deriving from it.[13]

SCHEME 3

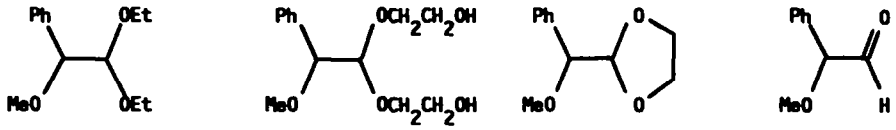


26 27 28

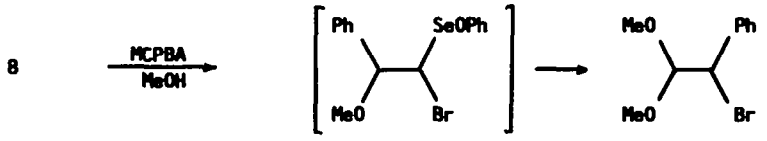
29 30

The conversion into the α-methoxy dimethyl acetals was also effected in the case of 1-bromo-1-octene **29** (Scheme 3). 1,1,2-Trimethoxy octane **30** was isolated in 45% yield from the reaction of **29** with PhSeCl and KNO_3 in MeOH at room temperature. The 1,1-dimethoxy-2-bromo octane was also present but it was not fully identified since it was contaminated by another unidentified product from which it could not be separated.

The α-halogenoselenide, 1-phenyl-1-methoxy-2-bromo-2-phenylselenenyl ethane **8**, was subjected to some deselenenylation reactions. As reported above its reaction with PhSeCl in MeOH occurred very easily and gave **4** in high yield. The use of other alcohols was then investigated. The same PhSeCl promoted solvolysis was much slower in ethanol than in methanol;[14] the 1-phenyl-1-methoxy-2,2-diethoxy ethane **31** was obtained in 85% yield after 3 h at 60 °C. In ethylen glycol[10,14] the same reaction occurred at room temperature for 4 h and gave the 1-phenyl-1-methoxy-2,2-(2-hydroxy) ethoxy ethane **32** (78%); when tetrahydrofuran was used as a co-solvent a mixture of **32** (31%) and **33** (51%) was obtained. The reaction of **8** with water/THF, in the presence of Na_2CO_3, was very slow;



31 **32** **33** **34**



5

complete conversion into the α-methoxyphenylacetaldehyde **34** (76%) was obtained after 20 h at 60 °C. Finally, the recently investigated conversion of alkyl phenyl selenides into alkyl methyl ethers by means of m-chloroperbenzoic acid in methanol,[10] was applied to **8**. This reaction, which has been shown to occur through the selenoxide, gave the expected substitution product with phenyl migration, i.e. compound **5**, which was isolated in 82% yield.

EXPERIMENTAL

Proton nmr spectra were recorded at 90 MHz on a Varian EM390 instrument. Carbon-13 spectra were recorded at 20.15 MHz on a Bruker WP80SY instrument operating in the Fourier transform mode with proton decoupling throughout. $CDCl_3$ was used as solvent and TMS as reference. Glc analyses were performed on a Hewlett Packard 5830A chromatograph with a 20 in., 10% UCW 982 column. Elemental analyses were carried out on a Carlo Erba Model 1106 Elemental Analyzer.

Commercial (E)-β-bromostyrene **3** was purified by column chromatography and distillation. 1-Phenyl-1-methoxy-2-phenylselenenyl ethane,[10] (E)-β-methoxystyrene **6**,[16] (E)-β-phenylselenenyl styrene **18**,[17] bromostilbene **26**,[18] and (Z)-1-bromo-1-octene **29**,[19] were prepared as described in the literature. The 1-phenyl-2-bromo-2-deuteroethylene **12** was obtained as a 4:1 mixture of the (Z)- and (E)- isomers (nmr and glc) starting from PhC≡CD[20] and following the procedure reported in the literature for the synthesis of (Z)-β-bromostyrene.[19]

General Procedure. To a solution of **3** (5 mmol) and PhSeCl (5 mmol) in methanol, silver or potassium nitrate (5 mmol) was added. The mixture was stirred at room temperature for 2 h. The progress of the reaction was monitored by tlc and glc. The resulting, strongly acid, brown reaction mixture was treated with styrene and stirred for 15 min. The mixture was poured on water and extracted with ether. The organic phase was washed with water, dried and evaporated. The

residue was analyzed by tlc, glc and nmr and chromatographed through a silica gel column using a 90:10 mixture of light petroleum and ether as eluant.

This work up and product isolation procedure was employed for all the other reactions described in this paper; only in the case of the preparation of **8** the reaction mixture was evaporated and the residue was directly subjected to column chromatography. Details on reaction conditions and yields are given under the Results and Discussion. Physical, spectral and analytical data of the isolated products are given below. Compound **27** was identical to a commercially available sample.

1-Phenyl-1,2,2-trimethoxy ethane, 4, oil. H-nmr δ 7.35 (s, 5 H); 4.35 (d, 1 H, J = 6.0 Hz); 4.15 (d, 1 H, J = 6.0 Hz); 3.45 (s, 3 H); 3.25 (s, 3 H); 3.2 (s, 3 H). ^{13}C-nmr δ 138.1, 128.2, 128.1, 128.0, 106.6, 84.0, 56.9, 55.6, 54.3. Found: C = 67.39, H = 8.18%. Requires: C = 67.33, H = 8.22%.

1-Phenyl-1-bromo-2,2-dimethoxy ethane, 5, oil (Litt.[21] b.p. 84 - 86 °C/0.4 mm). H-nmr δ 7.5 - 7.15 (m, 5 H); 4.95 (d, 1 H, J = 7.5 Hz); 4.75 (d, 1 H, J = 7.5 Hz); 3.5 (s, 3 H); 3.25 (s, 3 H). ^{13}C-nmr δ 138.1, 128.5, 128.3, 128.1, 106.0, 54.9, 54.6, 52.9.

1-Phenyl-1-phenylselenenyl-2,2-dimethoxy ethane, 7, oil. H-nmr δ 7.45 - 7.25 (m, 2 H); 7.25 - 7.0 (m, 8 H); 4.8 (d, 1 H, J = 6.0 Hz); 4.45 (d, 1 H, J = 6.0 Hz); 3.45 (s, 3 H); 3.3 (s, 3 H). ^{13}C-nmr δ 138.9, 135.6, 128.9, 128.6, 128.1, 127.7, 127.0, 106.6, 54.7, 54.3, 51.1. Found: C = 59.78, H = 5.69%. Requires: C = 59.82, H = 5.65%.

1-Phenyl-1-methoxy-2-bromo-2-phenylselenenyl ethane erythro, 8, oil. H-nmr δ 7.65 - 7.5 (m, 2 H); 7.5 - 7.15 (m, 8 H); 5.3 (d, 1 H, J = 4.5 Hz); 4.65 (d, 1 H, J = 4.5 Hz); 3.4 (s, 3 H). ^{13}C-nmr δ 138.0, 134.7, 129.2, 128.6, 128.3, 127.5, 86.5, 57.7, 54.8. In $CDCl_3$ solution, at room temperature for 15 h, this product is partially converted into another compound which might be the threo diasteroisomer; the treo compounds could not be separated. From the spectra of the mixture the following data could be obtained for the second compound: H-nmr δ 7.65 - 7.5 (m, 2 H); 7.5 - 7.0 (m, 8 H); 5.35 (d, 1 H, J = 4.5 Hz); 4.70 (d, 1 H, J = 4.5 Hz); 3.4 (s, 3 H). ^{13}C-nmr δ 138.1, 134.5, 129.0, 128.4, 128.2, 127.4, 87.4, 57.8, 55.7.

1-Phenyl-1,2-dimethoxy-2-phenylselenenyl ethane, 9, oil. H-nmr δ 7.55 - 7.15 (m, 10 H); 4.95 (d, 1 H, J = 4.5 Hz); 4.45 (d, 1 H, J = 4.5 Hz); 3.36 (s, 3 H); 3.33 (s, 3 H). ^{13}C-nmr δ 135.3, 128.9, 128.2, 128.1, 127.5, 96.0, 86.0, 57.8, 57.3. Found: C = 59.83, H = 5.68%. Requires: C = 59.82, H = 5.65%.

1-Phenyl-1,2-dimethoxy-2-bromo ethane, 11, oil. H-nmr δ 7.45 - 7.1 (m, 5 H); 5.05 (d, 1 H, J = 5.0 Hz); 4.55 (d, 1 H, J = 5.0 Hz); 3.4 (s, 3 H); 3.3 (s, 3 H). ^{13}C-nmr δ 135.0, 128.9, 128.2, 128.0, 127.5, 94.2, 86.7, 58.0, 57.7. Found: C = 48.98, H = 5.36%. Requires: C = 49.00, H = 5.35%.

1-Phenyl-1,2,2-trimethoxy-2-deutero ethane, 13, oil. H-nmr δ 7.4 (s, 5 H); 4.2 (s, 1 H); 3.5 (s, 3 H); 3.3 (s, 3 H); 3.2 (s, 3 H). ^{13}C-nmr δ 138.0, 128.0, 127.9, 107.2, 106.0, 104.8, 83.8, 56.8, 55.4, 54.1, Found: C = 67.02, H = 8.71%. Requires: C = 66.99, H = 8.69%.

1-Phenyl-1-bromo-2,2-dimethoxy-2-deutero ethane, 14, oil. H-nmr δ 7.5 - 7.25 (m, 5 H); 4.85 (s, 1 H); 3.5 (s, 3 H); 3.2 (s, 3 H). ^{13}C-nmr δ 137.8, 128.5, 128.4, 128.3, 107.2, 106.0, 104.8, 55.6, 54.6, 52.9. Found: C = 48.83, H = 5.70%. Requires: C = 48.80, H = 5.73%.

1-Phenyl-1,2,2-triethoxy ethane, 23, oil. H-nmr δ 7.4 - 7.15 (m, 5 H); 4.45 (d, 1 H, J = 4.8 Hz); 4.25 (d, 1 H, J = 4.8 Hz); 3.85 - 3.0 (m, 6 H); 1.25 (t, 3 H, J = 7.2 Hz); 1.15 (t, 3 H, J = 7.2 Hz); 0.95 (t, 3 H, J = 7.2 Hz). ^{13}C-nmr δ 139.2, 127.8, 127.7, 127.4, 104.8, 82.7, 64.6, 63.7, 62.4, 15.25, 15.2, 14.8. Found: C = 70.52, H = 9.28%. Requires: C = 70.56, H = 9.30%.

1-Phenyl-1-bromo-2,2-diethoxy ethane, 24, oil (Litt.[21] b.p. 96 °C/0.3 mm). H-nmr δ 7.5 - 7.2 (m, 5 H); 4.85 (d, 1 H, J = 6.5 Hz); 4.7 (d, 1 H, J = 6.5 Hz); 4.0 - 3.1 (m, 4 H); 1.25 (t, 3 H, J = 7.2

Hz); 1.0 (t, 3 H, J = 7.2 Hz). ^{13}C-nmr δ 138.0, 128.4, 128.3, 128.2, 104.8, 64.1, 63.3, 62.8, 15.2, 15.0.

1-Phenyl-1-methoxy-2,2-dibromo ethane, 25, oil. H-nmr δ 7.4 (s, 5 H); 5.7 (d, 1 H, J = 5.0 Hz); 4.5 (d, 1 H, J = 5.0 Hz); 3.4 (s, 3 H).[22]

2-Phenyl-2-bromo acetophenone, 28, m.p. 53 - 55 °C (Litt[23] m.p. = 54 - 55 °C). H-nmr δ 8.1 - 7.9 (m, 2 H); 7.7 - 7.2 (m, 8 H); 6.35 (s, 1 H). ^{13}C-nmr δ 191.0, 134.7, 133.5, 129.7, 129.1, 129.0, 128.9, 128.7, 50.9.

1,1,2-Trimethoxy octane, 30, oil. H-nmr δ 4.2 (d, 1 H, J = 6.0 Hz); 3.5 (s, 6 H); 3.45 (s, 3 H); 3.3 - 3.1 (m, 1 H); 1.7 - 1.1 (m, 10 H); 0.9 (t, 3 H, J = 7.2 Hz). ^{13}C-nmr δ 106.7, 81.6, 58.7, 55.4, 55.1, 31.9, 30.1, 29.6, 25.3, 22.7, 14.1. Found: C = 64.68, H = 11.87%. Requires: C = 64.67, H = 11.84%.

1-Phenyl-1-methoxy-2,2-diethoxy ethane, 31, oil. H-nmr δ 7.35 (s, 5 H); 4.45 (d, 1 H, J = 6.0 Hz); 4.15 (d, 1 H, J = 6.0 Hz); 3.9 - 3.35 (m, 4 H); 3.3 (s, 3 H); 1.25 (t, 3 H, J = 7.2 Hz); 0.95 (t, 3 H, J = 7.2 Hz). ^{13}C-nmr δ 138.5, 128.1, 128.0, 127.8, 104.8, 84.8, 64.0, 62.6, 57.2, 15.4, 15.0. Found: C = 69.59, H = 9.01%. Requires: C = 69.62, H = 8.99%.

1-Phenyl-1-methoxy-2,2-di(2-hydroxy)ethoxy ethane, 32, oil. H-nmr δ 7.4 (s, 5 H); 4.7 (d, 1 H, J = 6.6 Hz); 4.3 (d, 1 H, J = 6.6 Hz); 4.1 - 3.5 (m, 4 H); 3.35 (s, 3 H); 2.7 (s, 2 H). Found: C = 60.90, H = 7.89%. Requires: C = 60.93, H = 7.87%.

α-Methoxyphenylacetaldehyde ethylene acetal, 33, oil. H-nmr δ 7.4 (s, 5 H); 5.1 (d, 1 H, J = 4.5 Hz); 4.2 (d, 1 H, J = 4.5 Hz); 3.95 - 3.8 (m, 4 H); 3.35 (s, 3 H). Found: C = 68.05, H = 7.25%. Requires: C = 68.03, H = 7.27%.

α-Methoxyphenylacetaldehyde, 34, oil. H-nmr δ 9.6 (d, 1 H, J = 1.8 Hz); 7.35 (s, 5 H); 4.6 (d, 1 H, J = 1.8 Hz); 3.45 (s, 3 H).[24]

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

REFERENCES AND NOTES

1) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, and D. Bartoli, preceding paper.

2) Unpublished results from this laboratory.

3) B.M. Dilworth and M.A. Mckervey, **Tetrahedron**, **42**, 3731 (1986).

4) N. Petragnani, R. Rodriguez, and J.V. Comasetto, **J. Organomet Chem.**, **114**, 281 (1976).

5) W. Dumont, M. Sevrin, and A. Krief, **Angew. Chem. Int. Ed. Engl.**, **16**, 541 (1977).

6) J.V. Comasetto, J.T.B. Ferreira, C.A. Brandt and N. Petragnani, J. **Chem. Res.**, 212 (1982).

7) T.G. Back, and R.G. Kerr, **J. Organomet. Chem.**, **286**, 171 (1985).

8) D.J. Buckley and M.A. Mckervey, **J. Chem. Soc. Perkin Trans. I**, 2193 (1985).

9) H.J. Reich, C.P. Jasperse, and J.M. Renga. **J. Org. Chem.**, **51**, 2981 (1986).

10) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, and D. Bartoli, **Gazz. Chim. Ital.**, **117**, 423 (1987).

11) In the present case also the intermediate **10** can further react with PhSeCl to afford the selenonium chloride PhCH(OMe)CH(OMe)SeClPh^{+}Cl^{-} which then suffers solvolysis to give **4**. This however has no influence on the global process. The possibility that, under certain conditions, the reactive intermediate might be the selenium radical cation formed by electron fransfer from **9** and the oxidizing agent is presently under investigation.

12) C. Paulmier, "Selenium Reagents and Intermediates in Organic Synthesis", Pergamon Press, Oxford, 1986, p. 182.

13) Compound **17** could not be isolated and it is thus impossible to say if the attack of methanol at carbon-2 occurs on **16** or in the selenium stabilyzed carbocation PhCHBrC^{+}HSePh.

14) In agreement with the proposed mechanism the reaction should be slower in an alcohol having a lower dielectic constant than that of MeOH (see Ref. 10).

15) This procedure is now extensively used in our laboratory to effect the one-pot alkoxyselenenylation-deselenenylation process in alkenes, alkynes and enolizable ketones.[2]

16) M. Tiecco, D. Chianelli, L. Testaferri, M. Tingoli, and D. Bartoli, **Tetrahedron**, **42**, 4896 (1986).

17) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, and M. Montanucci, **Tetrahedron Lett.**, **25**, 4975 (1984).

18) A.G. Brook, K.H. Pannell, and D.G. Anderson, **J. Am. Chem. Soc.**, **90**, 4374 (1968).

19) H.C. Brown, and S.K. Gupta, **J. Am. Chem. Soc.**, **94**, 4370 (1972); H.C. Brown, T. Hamaoka, and N. Ravindran, **J. Am. Chem. Soc.**, **95**, 5786 (1973).

20) J.T. Wood, J.S. Arney, D. Cortes, and J.A. Berson, **J. Am. Chem. Soc.**, **100**, 3855 (1978).

21) J.E. Baldwin and L.E. Walker, **J. Org. Chem.**, **31**, 3985 (1966).

22) C.A. Kingsbury and G. Max, **J. Org. Chem.**, **43**, 3131 (1978).

23) E. Knoevenagel, **Chem. Ber.**, **21**, 1355 (1888).

24) R. Annunziata, M. Cinquini, F. Cozzi, A. Gilardi, S. Cardani, G. Poli and C. Scolastico, **J. Chem. Soc. Perkin Trans I**, 255, (1985).