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METHOXYCHLORINATION AND DIMETHOXYLATION OF ALKENES
THE REACTIONS OF SUBSTITUTED STYRENES WITH PHENYLSELENENYL CHLORIDE IN METHANOL

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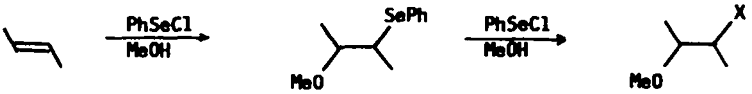
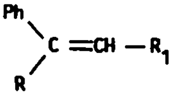
Abstract: The addition of PhSeCl to α- and β-substituted styrenes in methanol is regio- and stereospecific and affords the products of methoxyselenenylation. These compounds further react with PhSeCl to give the deselenenylation products. In the case of α-substituted styrenes, 1-methoxy, 2-chloroalkanes are produced, whereas with β-substituted styrenes the major reaction products are the 1,2-dimethoxyalkanes and the 2,2-dimethoxyalkanes in which phenyl migration has occurred. It is shown that these reactions proceed through the intermediate formation of the alkyl phenylselenium dichlorides, $PhCR(OMe)CHR_1SeCl_2Ph$, which evolve with different mechanisms depending on the structure of the starting alkenes.

The reactions of phenylselenenyl chloride with unsaturated compounds represent a very convenient way to introduce selenium into an organic molecule.[1] The use of hydroxylated solvents allows to effect the process of oxyselenenylation of alkenes, as well as of other unsaturated compounds.[1-3] The removal of the selenium containing mojety can then be effected in several ways. The most important process consists in the oxidation to selenoxides which easily give an elimination reaction by which a new carbon-carbon double bond is introduced into the molecule.[4] Oxidation to selenones is also a very useful reaction since the selenonyl is a very good leaving group and it can be substituted by a large number of nucleophiles.[5] Alternative deselenenylation processes, which however have not been fully investigated so far, consist in the transformation of alkyl aryl selenides into the corresponding radical anions[6] or radical cations[7] which give rise to fragmentation to eventually form the elimination or substitution products. Finally the removal of the selenium containing moiety can be also achieved through a preliminary transformation of the alkyl aryl selenides into selenonium salts by treatment with electrophilic reagents such as halogens.[8] The results reported in this paper indicate that the reactions of alkenes with excess phenylselenenyl chloride in methanol represent a very simple way to effect the one-pot methoxyselenenylation-deselenenylation processes by which methoxychloroalkanes (X = Cl) or dimethoxyalkanes (X = OMe) can be obtained.



The alkenes employed for the present investigation were the following α-substituted, **1a–c**, and β-substituted styrenes, **1d–g**:



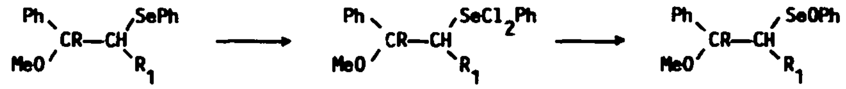
1

a: $R=R_1=H$
b: $R=Me$, $R_1=H$
c: $R=Ph$, $R_1=H$
d: $R=H$, $R_1=Ph$ (E)
e: $R=H$, $R_1=Ph$ (Z)
f: $R=H$, $R_1=Me$ (E)
g: $R=H$, $R_1=CH_2Ph$ (E)

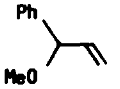
RESULTS AND DISCUSSION

In order to dispose of the possible intermediates which could intervene in the reactions of the styrenes with excess PhSeCl, some preliminary experiments were carried out to synthesize the addition products, 1-phenyl,1-methoxy,2-phenylseleneny1 alkanes, **2**, and their dichlorides **3**. The results are collected in Scheme 1 where reactions yields are also indicated.

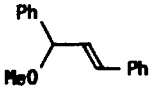
SCHEME 1



	2	3	4
a:	90 %	95 %	86 %
b:	87 %	92 %	88 %
c:	87 %	92 %	85 %
erythro, d:	65 %	--	80 %
threo, e:	70 %	90 %	84 %
erythro, f:	78 %	93 %	--
erythro, g:	91 %	87 %	--



5 (75%)



6 (81%)

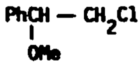
Compounds **2a–g** were prepared by stirring a solution of the alkenes with one molar equivalent of PhSeCl in methanol at room temperature. The desired products were obtained after 1 h. The only exception was that of the (Z)-stilbene which under these conditions afforded considerable amounts of the PhCHClCHPhSePh; the formation of this undesired compound was minimized by adding the stilbene dropwise to the solution of PhSeCl and stirring the reaction mixture for 5 h. In most cases products deriving from the further reactions of compounds **2d–g** (see below) were also present and the pure compounds could be obtained only after purification by column chromatography.[9] All these reactions were carried out under thermodinamically controlled conditions and were completely regiospecific;[10] a single regioisomer was in fact obtained from the alkenes **1a–c** and **1f–g**. The reactions with the β-substituted styrenes, **1d–g**, were also stereospecific and gave the products of the anti addition of the PhSe and MeO groups to the double bond; the (E)-alkenes gave the erythro and the (Z)-alkenes gave the threo diastereoisomers.[11]

Almost quantitative conversions of **2a–g** into the corresponding 1-phenyl-1-methoxy-2-phenylselenenyl alkanes dichlorides **3a–g** were effected by treatment with SO_2Cl_2 in CCl_4 at room temperature.[13,14] (Scheme 1). Only in the case of the 1,2-diphenyl-1-methoxy- 2-phenylselenenyl ethane erythro **2d** the dichloride **3d** could not be isolated; at room temperature in fact the only product obtained in this case was the PhCH(OMe)CHClPh erythro. The formation of **3d** in this reaction could be demonstrated by proton nmr by working at -30 °C; by increasing the temperature of the sample a rapid decomposition was observed with formation of the chloro derivative and phenylselenenyl chloride. As will be shown later in this paper the dichlorides **3** decompose in methanol to give the corresponding chloro and methoxy derivatives more or less easily depending on the structure of the alkyl group of the selenide. The same dichlorides **3**, dissolved in CCl_4 and treated with water at room temperature, were transformed into the corresponding selenoxides **4** (Scheme 1); in the case of **3d** this conversion was effected by adding water to the mixture resulting from the reaction of **2d** with SO_2Cl_2 at -30 °C. The selenoxides **4a–e** were relatively stable crystalline compounds, whereas **4f** and **4g** could not be isolated since they gave the well known elimination reaction to afford the alkenes **5** and **6**, respectively. A similar behaviour has been recently observed for the closely related β-chloroalkyl phenyl selenium dichlorides which on treatment with water gave vinyl and allyl chlorides.[14,15]

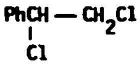
The selenoxides **4a** and **4b** were shown by nmr to be a mixture (about 2:1) of two diastereoisomers which could not be separated. The reactions of **3d** and **3e** were instead stereospecific, a single selenoxide, **4d** or **4e**, being obtained in both cases. Identical results were obtained when the selenoxides **4a–e** were prepared by oxidation of the corresponding selenides.[3,7,16]

The reactions of the alkenes **1a–g** with excess phenylselenenyl chloride (3 molar equivalents) in methanol give rise to the methoxyselenenylation products **2a–g** which further react with PhSeCl to afford the deselenenylation products; the course of this latter process depends on the structure of the starting alkenes. With α-substituted styrenes the only reaction products are those deriving by the replacement of the phenylselenenyl group by the chlorine. With β-substituted styrenes, on the contrary, the methoxychlorination products are formed in minute amounts, the major reaction products being those deriving by the solvolysis of **2d–g** with and without phenyl migration; under certain conditions, products of further transformation were also observed. In every case the selenium introduced in the first step is recovered in the second step.

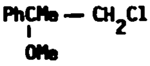
The following products have been isolated from the reactions of the styrenes **1a–c**:


$\underset{\text{OMe}}{\text{PhCH}}-\text{CH}_2\text{Cl}$

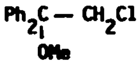
7


$\underset{\text{Cl}}{\text{PhCH}}-\text{CH}_2\text{Cl}$

8


$\underset{\text{OMe}}{\text{PhCMe}}-\text{CH}_2\text{Cl}$

9

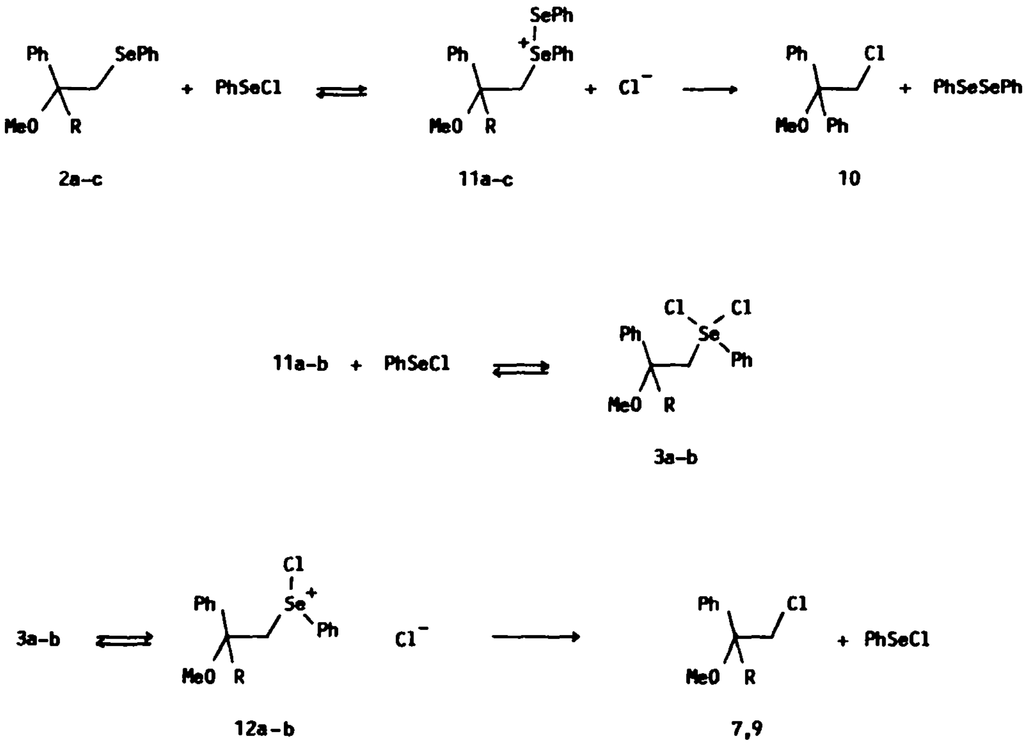

$\underset{\text{OMe}}{\text{Ph}_2\text{C}}-\text{CH}_2\text{Cl}$

10

Nmr examination of the reaction mixtures just after the mixing of the reagents at room temperature showed that **1a** and **1b** were completely transformed into the dichlorides **3a** and **3b**, respectively. Under the same conditions, **1c** was instead converted into **10**; no indications of the formation of **3c** could be obtained, not even when the reaction was run at -30 °C. The reaction mixture containing the dichloride **3a** remained unchanged in methanol at room temperature; the transformation into a mixture of **7** (55%) and **8** (27%) required 12 h at reflux. The reaction mixture containing the corresponding methyl derivative **3b** gave **9** (90%) after 4 h at room temperature. Identical results were obtained from the reactions of the addition products **2a–c** with 2 moles of PhSeCl. Pure **3a** and **3b**, prepared as indicated in Scheme 1, were stable in methanol at room temperature and gave **7**, **8** and **9** after reflux for 12 and 4 h, respectively. Similarly, **3c** was stable at room temperature and gave **10** only after 1 h at reflux. This latter result seems to indicate that **3c** does not form during the reaction of **1c** with PhSeCl. From these decompositions of **3a–c** in methanol phenylselenenyl chloride was also formed.[17]

The observed results might be explained assuming that the initially formed selenides **2a–c** react with PhSeCl to afford selenonium chlorides of type **11** (Scheme 2)[18] and that these can further react to give the dichlorides **3**.[13] In methanol, these dichlorides can be assumed to be in equilibrium with the corresponding selenonium chlorides **12**. Compounds **7**, **9** and **10** can thus form through the displacement of the selenonium group by the chloride anion according to an S_N2 process. However, the above described observations seem to indicate that in the case of **1a** and **1b** this process occurs on **12a** and **12b**, whereas in the case of **1c**, where the dichloride **3c** was not observed, the substitution takes place on **11c**.[19] The formation of **8** cannot be easily rationalized.

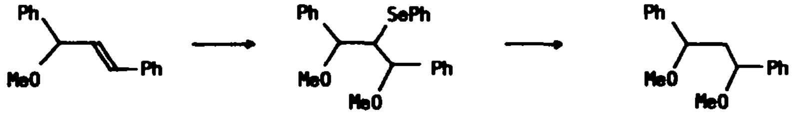
SCHEME 2



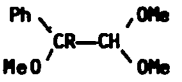
Also in the case of the β-substituted styrenes **1d–g** the reactions with three moles of PhSeCl gave the dichlorides **3**. This could be evidenced by nmr just after the mixing of the reagents at room temperature. The dichloride **3d**, deriving from (E)-stilbene, reacted very rapidly and its spectrum could be recorded only by working at -30 °C. The reaction with (Z)-stilbene afforded a mixture of **3e** and of PhCHClCHPhSeCl$_2$Ph; this latter product however gradually reverted to the starting compounds and the reaction was complete after 3 h. In the case of the two β-alkylstyrenes, **1f** and **1g**, the dichlorides, **3f** and **3g**, were stable at room temperature and the reaction mixtures were therefore refluxed for 2 h. The results obtained from these experiments are collected in Scheme 3. Similar results were obtained from the reactions of the addition products **2d–g** with two moles of PhSeCl and from the decomposition of the dichlorides **3e–g** in methanol.

SCHEME 3

3d^{a}	**13**(7%)^{a}	**14**(28%)^{c}+ **15**(8%)^{d}	**16**(45%)
3e^{b}	**17**(7%)^{b}	**15**(20%) + **14**(10%)	**16**(50%)
3f^{a}		**18**(15%)^{a}+ **19**(15%)^{b}	**20**(25%)
3g^{a}	**21**(15%)^{a}	**22**(10%)^{a}	**23**(41%)



6 **24**(17%) **25**

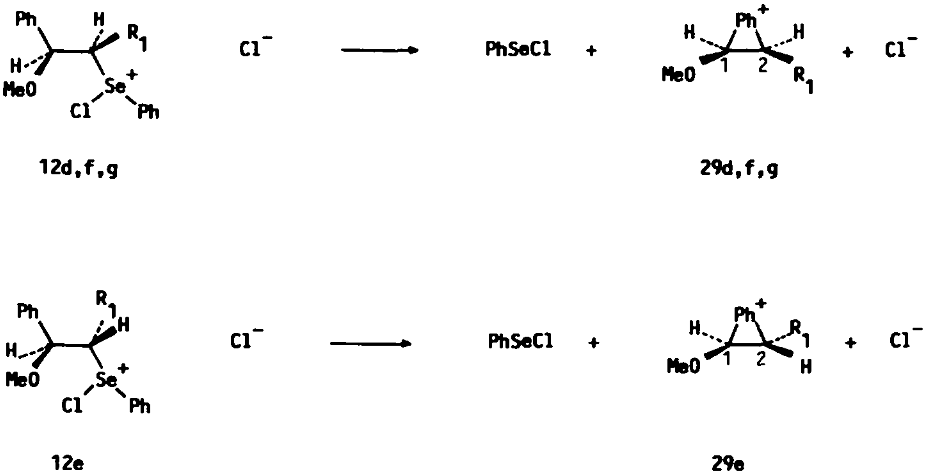


26: R = Ph; **27**: R = Me; **28**: R = CH$_2$Ph

a: erythro; b: threo; c: meso; d: dl

In this case therefore, after the rapid formation of the dichlorides **3d–g**, two substitution processes are going on concurrently, with the replacement of the phenylselenenyl group by both the chlorine and the methoxy groups. In the first case the substitution occurs with retention of configuration; on the contrary, the solvolysis is not completely stereospecific and moreover it mainly evolves towards the products of substitution with phenyl migration. These results indicate that with the dichlorides **3d–g** the reaction proceeds through the initial ionization of the carbon selenium bond. Therefore, it can be suggested that the dichlorides **3d–g** equilibrate with the corresponding selenonium chlorides **12d–g**; phenyl assisted elimination of PhSeCl could afford the phenonium ions intermediates **29d,f,g** and **29e** (Scheme 4). Attack by the chloride anion at carbon-2 leads to the chloromethoxy derivatives **13**, **17** and **21**. Attack by methanol at the same carbon gives the 1,2-dimethoxyalkanes **14**, **15**, **18** and **22**, whereas attack at carbon-1, accompanied by phenyl migration, affords the 2,2-dimethoxyalkanes **16**, **20**, and **23**.

SCHEME 4



The relative importance of the two substitution processes is a function of the concentration; in fact, when the reaction of the (E)-stilbene was carried out in dilute solutions the formation of the 1,2-diphenyl-1-methoxy-2-chloro ethane **13** could be completely suppressed.[20]

From the reaction of **1g** with excess PhSeCl a further product was isolated in considerable amounts. This compound was identified as the 1,3-diphenyl-1,3-dimethoxy-2-phenylselenenyl propane **24** since it could also be obtained from the reaction of **6** with PhSeCl in methanol, and moreover, by reduction with nickel Raney, it gave the deselenenylated compound **25** (Scheme 3). The formation of **24** can be explained assuming that the intermediate **12g** can also evolve by elimination to give the alkene **6** which is then trapped by the PhSe cations.[21] Indeed the 1,3-diphenyl-3-methoxy-1-propene, **6**, could also be isolated as a by-product from an experiment carried out with **1g** and two molar equivalents of PhSeCl. The dimethyl acetals **16**, **20**, and **23** were stable under the experimental conditions described above. However, when the reaction mixtures were kept at reflux for 5-6 h they were completely consumed and the trimethoxyalkanes **26**, **27** and **28** were obtained (Scheme 3). As a possible explanation for the formation of these compounds it can be suggested that the acetals can give rise to an elimination reaction to afford the alkenes PhCR=CHOMe which then react with PhSeCl in a way similar to that observed in the case of **1d-g**; thus, methoxyselenenylation followed by methoxydeselenenylation can eventually lead to the observed products.

The results described in this paper indicate that the reaction with excess phenylselenenyl chloride represents a convenient procedure to effect the one-pot alkoxychlorination of terminal alkenes or the dialkoxylation of 1,2-substituted alkenes. Further work is presently under way to extend the scope of this reaction; naturally occurring and variously substituted alkenes, alkynes and enolizable ketones give rise to interesting conversions. Experiments are also in progress to find appropriate conditions to effect the alkoxyselenenylation - deselenenylation process using a precursor of the PhSe cations in catalytic amounts.

EXPERIMENTAL

Structural attributions were made by proton, carbon-13, mass spectra and by elemental analyses. 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. Mass spectra were recorded with a Hewlett-Packard 5970B Mass Selective Detector connected with an HP 5890A gaschromatograph. 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.[22,23] The values reported below refer only to the prominent picks; for the ions containing selenium only the pick arising from the selenium-80 isotope is given. Elemental analyses were carried out on a Carlo Erba Model 1106 Elemental Analyzer. Glc analyses were performed on a Hewlett-Packard 5830A chromatograph with a 20 in., 10% UCW 982 column.

Compounds **1a-1e** were commercially available; 1-phenyl-1-propene, **1f**,[24] and 1,3-diphenyl-1-propene, **1g**,[25] were prepared as described in the literature. 1-Phenyl-1-methoxy-2-phenylselenenyl ethane, **2a**, 2-phenyl-2-methoxy-1-phenylselenenyl propane, **2b**, 1,1-diphenyl-1-methoxy-2-phenylselenenyl ethane, **2c** and the corresponding selenoxides **4a**, **4b** and **4c** have already been described.[3]

Reactions of Styrenes 1a-g with PhSeCl

A solution of the styrene (5 mmol) and of PhSeCl (5 mmol) in methanol (15 ml) was stirred at room temperature for about 1 h (5 h in the case of **1e**). The progress of the reaction was monitored by tlc. The reaction mixture was poured on water and extracted with ether. After the usual work up the residue was chromatographed through a silica gel column using light petroleum as eluant. Reaction yields are reported in Scheme 1; physical and spectral data of new compounds are reported below.

1,2-Diphenyl-1-methoxy-2-phenylselenenyl ethane, erythro, 2d, oil. H-nmr δ 7.3 - 6.9 (m, 10 H); 4.65 (d, 1 H, J = 6.0 Hz); 4.4 (d, 1 H , J = 6.0 Hz); 3.2 (s, 3 H). ^{13}C-nmr δ 139.4, 139.2, 134.8, 129.2, 128.6, 128.3, 128.2, 127.9, 127.7, 127.6, 127.3, 126.7, 86.3, 57.3, 55.2. Mass, m/e 306 (1), 121 (100). Found: C = 68.71, H = 5.53%. Requires: C = 68.66, H = 5.49%.

1,2-Diphenyl-1-methoxy-2-phenylselenenyl ethane, threo, 2e, oil. H-nmr δ 7.35 - 7.15 (m, 2 H); 7.2br (s, 5 H); 7.15 - 6.9 (m, 3 H); 7.0br (s, 5 H); 4.6 (d, 1 H, J = 7.5 Hz); 4.5 (d, 1 H, J = 7.5 Hz); 3.3 (s, 3 H). ^{13}C-nmr δ 140.0, 139.5, 135.5, 128.9, 128.3, 128.0, 127.8, 127.7, 127.3, 126.7, 87.4, 57.0, 56.3. Mass, m/e 368 (4), 247 (7), 211 (32), 179 (21), 178 (20), 121 (100), 105 (18). Found: C = 68.48, H = 5.51%. Requires: C = 68.66, H = 5.49%.

1-Phenyl-1-methoxy-2-phenylselenenyl propane, erythro, 2f, oil. H-nmr δ 7.6 - 7.4 (m, 2 H); 7.3 - 7.1 (m, 8 H); 4.4 (d, 1 H, J = 4.5 Hz); 3.45 (dq, 1 H, J = 4.5 and 7.2 Hz); 3.3 (s, 3 H); 1.35 (d, 3 H, J = 7.2 Hz). ^{13}C-nmr δ 139.8, 134.7, 129.0, 128.3, 127.8, 127.4, 127.1, 86.5, 57.6, 45.8, 16.5. Mass, m/e 306 (4), 237 (5), 205 (1), 185 (2), 149 (7), 121 (100). Found: C = 63.05, H = 5.91%. Requires: C = 62.95, H = 5.94%.

1,3-Diphenyl-1-methoxy-2-phenylselenenyl propane, erythro, 2g, m.p. = 62 - 64 °C. H-nmr δ 7.25 (s, 5 H); 7.2 - 6.9 (m, 10 H); 4.38 (d, 1 H, J = 5.4 Hz); 3.5 (ddd, 1 H, J = 4.2, 5.4 and 9.0 Hz); 3.25 (s, 3 H); 3.15 (dd, 1 H, J = 4.2 and 15.0 Hz); 2.9 (dd, 1 H, J = 9.0 and 15.0 Hz). ^{13}C-nmr δ

139.75, 139.6, 134.7, 129.4, 128.65, 128.2, 128.1, 127.7, 127.3, 127.1, 126.2, 85.9, 57.4, 54.8, 36.5. Mass, m/e 382 (15), 225 (4), 194 (45), 157 (24), 121 (100), 91 (55), 77 (38). Found: C = 69.15, H = 5.79%. Requires: C = 69.29, H = 5.81%.

To a solution of **2a-g** (1.5 mmol), in carbon tetrachloride, SO_2Cl_2 was added dropwise at room temperature and the mixture was stirred for 0.5 h. The solvent was evaporated and the residue was taken up with CCl_4. Evaporation of the solvent left a residue which was not subjected to further purification. In the case of **2d** the reaction was carried out at - 30 °C and directly analyzed by nmr. Reaction yields are given in Scheme 1; physical and spectral data are reported below.

1-Phenyl-1-methoxy-2-phenylselenenyl ethane dichloride, 3a, m.p. = 127 - 130 °C. H-nmr δ 8.0 - 7.75 (m, 2 H); 7.55 - 7.3 (m, 8 H); 5.30 (dd, 1 H, J = 4.5 and 10.5 Hz); 4.6 (t, 1 H, J = 10.5 Hz); 4.35 (dd, 1 H, J = 4.5 and 10.5 Hz); 3.4 (s, 3 H). ^{13}C-nmr δ 137.5, 131.3, 129.7, 129.4, 129.2, 129.1, 127.1, 78.4, 70.5, 57.4. Mass, m/e 294 (1), 292 (5), 157 (5), 121 (100), 77 (31). Found: C = 49.70, H = 4.52%. Requires: C = 49.75, H = 4.45%.

2-Phenyl-2-methoxy-1-phenylselenenyl propane dichloride, 3b, oil. H-nmr δ 7.9 - 7.7 (m, 2 H); 7.7 - 7.2 (m, 8 H); 4.75 (d, 1 H, J = 10.5 Hz); 4.55 (d, 1 H, J = 10.5 Hz); 3.25 (s, 3 H); 2.15 (s, 3 H).Mass, m/e 306 (2), 157 (3), 135 (100), 91 (12), 77 (14).[26]

1,1-Diphenyl-1-methoxy-2-phenylselenenyl ethane dichloride, 3c, oil. H-nmr δ 7.95 - 7.7 (m, 2 H); 7.6 - 7.3 (m, 13 H); 5.3 (s, 2 H); 3.2 (s, 3 H). Mass, m/e 368 (2), 197 (100), 105 (22), 77 (18).[26]

1,2-Diphenyl-1-methoxy-2-phenylselenenyl ethane dichloride, erythro, 3d, oil. H-nmr δ (CCl_4) 7.7 - 7.0 (m, 15 H); 5.95 (d, 1 H, J = 8.4 Hz); 5.55 (d, 1 H, J = 8.4 Hz); 3.25 (s, 3 H).[26]

1,2-Diphenyl-1-methoxy-2-phenylselenenyl ethane dichloride, threo, 3e, oil. H-nmr δ 7.6 - 7.0 (m, 15 H); 6.25 (d, 1 H, J = 10.5 Hz); 5.5 (d, 1 H, J = 10.5 Hz); 3.4 (s, 3 H). ^{13}C-nmr δ 136.6, 132.4, 131.0, 130.7, 130.6, 129.8, 129.3, 128.8, 128.7, 128.3, 128.1, 127.7, 93.5, 82.4, 56.9. Mass, m/e 368 (5), 211 (36), 179 (19), 178 (19), 167 (11), 121 (100), 105 (17).

1-Phenyl-1-methoxy-2-phenylselenenyl propane dichloride, erythro, 3f, oil. H-nmr δ 8.05 - 7.85 (m, 2 H); 7.55 - 7.1 (m, 8 H); 5.45 (d, 1 H, J = 4.2 Hz); 4.8 (dq, 1 H, J = 4.2 and 6.9 Hz); 3.45 (s, 3 H); 1.65 (d, 3 H, J = 6.9 Hz). ^{13}C-nmr δ 131.2, 130.2, 129.6, 128.7, 127.0, 81.9, 76.9, 57.8, 12.7. Mass, m/e 306 (11), 185 (2), 149 (11), 121 (100).

1,3-Diphenyl-1-methoxy-2-phenylselenenyl propane dichloride, erythro, 3g, m.p. = 95 - 98 °C. H-nmr δ 7.85 - 7.65 (m, 2 H); 7.65 - 6.7 (m, 13 H); 5.55 (d, 1 H, J = 3.9 Hz); 5.05 (ddd, 1 H, J = 3.9, 4.5 and 6.6 Hz); 3.8 (dd, 1 H, J = 6.6 and 16.5 Hz); 3.5 (dd, 1 H, J = 4.5 and 16.5 Hz); 3.45 (s, 3 H). ^{13}C-nmr δ 138.2, 137.3, 131.3, 131.0, 129.2, 129.0, 128.8, 128.3, 127.2, 126.5, 83.9, 83.0, 58.1, 33.0. Found: C = 58.36, H = 4.93%. Requires: C = 58.42, H = 4.90%.

A solution of the dichlorides **3a-g** in CCl_4 was shaken with water for 15 minutes. The organic layer was washed with sodium bicarbonate and then with water. Evaporation of the solvent left a residue which was constituted by the crystalline selenoxides in the cases of **2a-e**, or by the oleous alkenes in the case of **2f** and **2g**. The selenoxides were purified by washing with light petroleum, whereas the alkenes where chromatographed through a silica gel column using light petroleum as eluant. The selenoxide **4d** was obtained by adding water to the reaction mixture of **2d** and SO_2Cl_2 kept at - 30 °C. Reaction yields are given in Scheme 1; physical and spectral data of new compounds are reported below.

1,2-Diphenyl-1-methoxy-2-phenylseleninyl ethane, erythro, 4d, m.p. 94 - 96 °C. H-nmr δ 7.4 - 6.9 (m, 15 H); 5.3 (d, 1 H, J = 4.0 Hz); 3.8 (d, 1 H, J = 4.0 Hz); 3.5 (s, 3 H). Mass, m/e 210 (100), 179 (13), 167 (64), 152 (48), 105 (45), 91 (46). Found: C = 65.72, H = 5.29%. Requires: C = 65.80, H = 5.26%.[26]

1,2-Diphenyl-1-methoxy-2-phenylseleninyl ethane, threo, 4e, m.p. 100 - 103 °C. H-nmr δ 7.4 - 6.7 (m, 15 H); 4.95 (d, 1 H, J = 10.8 Hz); 4.1 (d, 1 H, J = 10.8 Hz); 3.4 (s, 3 H). ^{13}C-nmr δ 138.1, 130.4, 129.4, 128.6, 128.4, 128.2, 127.9, 127.6, 127.4, 126.0, 81.6, 74.2, 56.9. Mass, m/e 368 (3), 211 (40), 179 (23), 178 (23), 165 (13), 121 (100), 77 (17). Found: C = 65.75, H = 5.31%. Requires: C = 65.80, H = 5.26%.

3-Phenyl-3-methoxy-1-propene, 5, oil. H-nmr δ 7.3br (s, 5 H); 5.9 (ddd, 1 H, J = 6.6, 10.0 and 17.4 Hz); 5.25 (ddd, 1 H, J = 1.0, 1.8 and 17.4 Hz); 5.15 (ddd, 1 H, J = 1.0, 1.8 and 10.0 Hz); 4.6 (dt, 1 H, J = 1.0 and 6.6 Hz); 3.35 (s, 3 H). ^{13}C-nmr δ 138.8, 128.4, 127.6, 126.8, 116.2, 84.7, 56.3. Mass, m/e 147 (17), 132 (4), 105 (100), 89 (8), 77 (73). Found: C = 80.97, H = 8.19%. Requires: C = 81.05, H = 8.16%.

1,3-Diphenyl-3-methoxy-1-propene, 6, oil. H-nmr δ 7.45 - 7.05 (m, 10 H); 6.6 (d, 1 H, J = 15.9 Hz); 6.25 (dd, 1 H, J = 6.3 and 15.9 Hz); 4.8 (d, 1 H, J = 6.3 Hz); 3.4 (s, 3 H). ^{13}C-nmr δ 136.8, 131.6, 130.4, 128.6, 127.8, 127.0, 126.7, 84.4, 56.5. Mass, m/e 224 (11), 192 (100), 165 (16), 115 (11). Found: C = 85.79, H = 7.24%. Requires: C = 85.68, H = 7.19%.

Reactions of Styrenes 1a-g with excess PhSeCl

PhSeCl (15 mmol) was added to a stirred solution of the styrene (5 mmol) in methanol (25 ml) at room temperature. A small aliquot of the reaction mixture was immediately evaporated and analyzed by nmr. The styrenes **1a**, **1b**, **1e** (see Results and Discussion), **1f** and **1g** were completely transformed into the dichlorides **3** of the corresponding addition products **2**, whereas **1c** and **1d** were transformed into the final reaction products. The reaction mixture deriving from **1e** was stirred at room temperature for 3 h, whereas those deriving from **1a**, **1b**, **1f** and **1g** were refluxed for 12, 4, 2, and 2 h, respectively. The progress of the reaction was monitored by glc and nmr. The reaction mixture was poured on water and extracted with ether. The organic layer was washed, dried over sodium sulphate and evaporated. The residue was chromatographed through a silica gel column using mixtures of light petroleum and ether (from 98:2 to 90:10) as eluant. Diphenyl diselenide (70 - 80%) was obtained in every case by evaporation of the first fractions.

The reactions of compounds **2a-g** (1.5 mmol) with PhSeCl (3 mmol) in methanol (10 ml) and the decomposition of the dichlorides **3a-c** and **3e-g** (1.5 mmol) in methanol (10 ml) were carried out in a similar way.

Reaction products and yields are given under the Results and Discussion section and in Scheme 3; physical and spectral data are reported below.

1-Phenyl-1-methoxy-2-chloro ethane, 7, oil (Litt.[27] b.p. 79 - 82 °C/4mm). H-nmr δ 7.4br (s, 5 H); 4.35 (dd, 1 H, J = 5.5 and 8.0 Hz); 3.65 (dd, 1 H , J = 8.0 and 12.5 Hz); 3.55 (dd, 1 H, J = 5.5 and 12.5 Hz); 3.3 (s, 3 H). ^{13}C-nmr δ 138.7, 129.0, 127.3, 126.9, 83.7, 57.0, 48.0.

1-Phenyl-1,2-dichloro ethane, 8, oil (Litt.[28] b.p. 99 °C/8mm). H-nmr δ 7.4br (s, 5 H); 5.0 (dd, 1 H, J = 5.5 and 8.0 Hz); 4.0 (dd, 1 H, J = 5.5 and 12.5 Hz); 3.95 (dd, 1 H, J = 8.0 and 12.5 Hz). ^{13}C-nmr δ 128.7, 128.6, 128.4, 61.8, 48.3.

2-Phenyl-2-methoxy-1-chloro propane, 9, oil. H-nmr δ 7.4br (s, 5 H); 3.7 (d, 1 H, J = 11.4 Hz); 3.6 (d, 1 H, J = 11.4 Hz); 3.15 (s, 3 H); 1.7 (s, 3 H). ^{13}C-nmr δ 141.8, 128.4, 127.8, 126.5, 78.7, 53.2, 50.8, 20.8. Mass, m/e 169 (2), 135 (100), 105 (13), 91 (17), 77 (24). Found: C = 65.10, H = 7.07%. Requires: C = 65.04, H = 7.10%.

1,1-Diphenyl-1-methoxy-2-chloro ethane, 10, oil. H-nmr δ 7.5 - 7.1 (m, 10 H); 4.3 (s, 2 H); 3.2 (s, 3 H). ^{13}C-nmr δ 142.5, 128.0, 127.4, 127.1, 81.9, 50.7, 48.6. Mass, m/e 246 (1), 197 (100), 178 (10), 152 (6), 105 (50), 77 (46). Found: C = 73.06, H = 6.16%. Requires: C = 73.02, H = 6.13%.

1,2-Diphenyl-1-methoxy-2-chloro ethane, erythro, 13, m.p. 95 - 97 °C. H-nmr δ 7.35 - 7.1 (m, 10 H); 4.95 (d, 1 H, J = 6.6 Hz); 4.5 (d, 1 H, J = 6.6 Hz); 3.2 (s, 3 H). ^{13}C-nmr δ 138.4, 137.9, 128.4, 128.3, 128.2, 128.0, 87.3, 65.45, 57.4. Mass, m/e 210 (8), 178 (5), 165 (10), 121 (100). Found: C = 73.10, H = 6.09%. Requires: C = 73.02, H = 6.13%.

1,2-Diphenyl-1,2-dimethoxy ethane, meso, 14, m.p. 143 - 144 °C (Litt.[29] 137 - 139 °C). H-nmr δ 7.4 - 7.1 (m, 5 H); 4.3 (s, 1 H); 3.2 (s, 3 H). ^{13}C-nmr δ 138.6, 128.0, 127.8, 127.6, 87.0, 57.1. Mass, m/e 211 (1), 165 (2), 121 (100), 105 (7), 91 (14).

1,2-Diphenyl-1,2-dimethoxy ethane, dl, 15, m.p. 88 - 91 °C (Litt.[29] 90 - 92 °C). H-nmr δ 7.3 - 6.9 (m, 5 H); 4.35 (s, 1 H); 3.3 (s, 3 H). ^{13}C-nmr δ 138.3, 127.85, 127.8, 127.6, 87.7, 57.1. Mass, m/e 211 (1), 165 (2), 121 (100), 105 (9), 91 (17).

1,1-Diphenyl-2,2-dimethoxy ethane, 16, oil (Litt.[29] b.p. 138 °C/0.55 mm). H-nmr δ 7.35 - 7.1 (m, 10 H); 4.95 (d, 1 H, J = 7.5 Hz); 4.25 (d, 1 H, J = 7.5 Hz); 3.3 (s, 6 H). ^{13}C-nmr δ 141.1, 128.7, 128.2, 126.3, 106.5, 87.0, 53.95. Mass, m/e 241 (4), 210 (15), 165 (16), 75 (100).

1,2-Diphenyl-1-methoxy-2-chloro ethane, threo, 17, oil. H-nmr δ 7.3br (s, 5 H); 7.15br (s, 5 H); 4.95 (d, 1 H, J = 7.5 Hz); 4.45 (d, 1 H, J = 7.5 Hz); 3.35 (s, 3 H). ^{13}C-nmr δ 137.7, 128.4, 128.2, 127.8, 127.5, 87.9, 66.9, 57.5. Mass, m/e 211 (1), 178 (2), 165 (2), 121 (100), 105 (7), 91 (13), 77 (21). Found: C = 72.97, H = 6.16%. Requires: C = 73.02, H = 6.13%.

1-Phenyl-1,2-dimethoxy propane, erythro, 18, oil. H-nmr δ 7.35 (s, 5 H); 4.2 (d, 1 H, J = 4.8 Hz); 3.45 (dq, 1 H, J = 4.8 and 6.3 Hz); 3.35 (s, 6 H); 1.15 (d, 3 H, J = 6.3 Hz). ^{13}C-nmr δ 139.3, 128.1, 127.5, 86.2, 80.7, 57.3, 57.0, 14.4. Mass, m/e 180 (1), 165 (1), 135 (17), 121 (100), 105 (12), 91 (19), 77 (28), 59 (29). Found: C = 73.28, H = 8.87%. Requires: C = 73.30, H = 8.95%.

1-Phenyl-1,2-dimethoxy propane, threo, 19, oil. H-nmr δ 7.45 - 7.2 (m, 5 H); 4.1 (d, 1 H, J = 6.9 Hz); 3.55 (quintet, 1 H, J = 6.9 Hz); 3.45 (s, 3 H); 3.25 (s, 3 H); 0.9 (d, 3 H, J = 6.9 Hz). ^{13}C-nmr δ 128.2, 127.8, 127.7, 87.5, 80.1, 57.3, 57.1, 15.7. Mass, m/e 180 (1), 149 (1), 121 (100), 105 (10), 91 (20), 77 (24), 59 (31). Found: C = 73.33, H = 8.96%. Requires: C = 73.30, H = 8.95%.

1,1 Dimethoxy-2-phenyl propane, 20, oil. H-nmr δ 7.3 (s, 5 H); 4.35 (d, 1 H, J = 6.9 Hz); 3.4 (s, 3 H); 3.25 (s, 3 H); 3.0 (quintet, 1 H, J = 6.9 Hz); 1.3 (d, 3 H, J = 6.9 Hz). ^{13}C-nmr δ 143.3, 128.4, 128.1, 126.5, 108.9, 54.6, 54.2, 43.2, 16.9. Mass, m/e 179 (1), 149 (9), 134 (2), 117 (7), 105 (12), 91 (10), 75 (100). Found: C = 73.26, H = 8.89%. Requires: C = 73.30, H = 8.95%.

1,3-Diphenyl-1-methoxy-2-chloro propane, erithro, 21, oil. H-nmr δ 7.45 - 7.1 (m, 10 H); 4.4 - 4.15 (m, 1 H); 3.35 (s, 3 H); 3.6 - 2.9 (m, 3 H). ^{13}C-nmr δ 137.8, 134.7, 129.6, 128.4, 128.3, 127.8, 126.6, 86.2, 65.8, 57.4, 39.3. Mass, 224 (35), 192 (24), 121 (100), 91 (23), 77 (23). Found: C = 73.67, H = 6.60%. Requires: C = 73.70, H = 6.57%.

1,3-Diphenyl-1,2-dimethoxy propane, erithro, 22, oil. H-nmr δ 7.35br (s, 5 H); 7.2br (s, 5 H); 4.05 (d, 1 H, J = 6.0 Hz); 3.5 (ddd, 1 H, J = 3.6, 6.0 and 7.8 Hz); 3.25 (s, 3 H); 3.0 (s, 3 H); 2.95 (dd, 1 H, J = 3.6 and 14.1 Hz); 2.75 (dd, 1 H, J = 7.8 and 14.1 Hz). ^{13}C-nmr δ 139.4, 129.6, 128.1, 127.8, 125.9, 86.3, 85.0, 58.9, 56.9, 37.1. Mass, m/e 224 (6), 192 (4), 135 (86), 121 (100), 105 (28), 91 (65), 77 (35). Found: C = 79.63, H = 7.91%. Requires: C = 79.66, H = 7.86%.

1,1-Dimethoxy-2,3-diphenyl propane, 23, oil. H-nmr δ 7.3 - 6.8 (m, 10 H); 4.5 (d, 1 H, J = 5.7 Hz); 3.8 - 2.7 (m, 3 H); 3.45 (s, 3 H); 3.25 (s, 3 H). ^{13}C-nmr δ 140.5, 140.2, 129.3, 129.0, 128.1, 128.0, 126.5, 125.8, 107.5, 54.5, 54.4, 51.2, 37.8. Mass, m/e 224 (39), 192 (17), 75 (100). Found: C = 79.67, H = 7.84%. Requires: C = 79.66, H = 7.86%.

1,3-Diphenyl-1,3-dimethoxy-2-phenylselenenyl propane, 24, m.p. 87 - 89 °C. H-nmr δ 7.6 - 7.0 (m, 10 H); 6.95 - 6.6 (m, 3 H); 6.4 - 6.2 (m, 2 H); 5.15 (d, 1 H, J = 1.8 Hz); 4.5 (d, 1 H, J =10.2

Hz); 3.45 (s, 3 H); 3.3 (s, 3 H); 3.05 (dd, 1 H, J = 1.8 and 10.2 Hz). ^{13}C-nmr δ 140.8, 140.1, 134.4, 128.6, 127.9, 127.8 127.7, 127.6, 127.4, 127.2, 126.7, 85.0, 80.8, 63.4, 57.5, 56.8. Mass, m/e 412 (5), 314 (12), 260 (10), 192 (100), 121 (69), 77 (41). Found: C = 67.00, H = 5.91%. Requires: C = 67.15, H = 5.88%.

This compound was also obtained, in 82% yield, from the reaction of **6** (1 mmol) with PhSeCl (1 mmol) in methanol at room temperature for 0.5 h.

From the reaction of **24** in ethanol with Raney nickel a single product was obtained, which was identified as the **1,3-diphenyl-1,3-dimethoxy propane, 25**, (75%), m.p. 62 - 64 °C by comparison with an authentic sample prepared as described below.

When the reaction mixtures deriving from **1d**, **1e**, **1f** and **1g** were refluxed for 5 h the acetals **16**, **20**, and **23** were consumed and together with the other products indicated in Scheme 3, the following compounds were isolated with yields indicated in parentheses.

1,1-Diphenyl-1,2,2-trimethoxy ethane, 26 (38%), oil. H-nmr δ 7.5 - 7.15 (m, 10 H); 4.8 (s, 1 H); 3.45 (s, 6 H); 3.2 (s, 3 H); ^{13}C-nmr δ 141.2, 129.3, 127.4, 127.2, 110.8, 85.7, 57.8, 53.0. Mass, m/e 241 (1), 197 (13), 165 (6), 105 (19), 75 (100). Found: C = 75.00, H = 7.37%. Requires: C = 74.98, H = 7.40%.

1,1,2-Trimethoxy-2-phenyl propane, 27 (22%), oil. H-nmr δ 7.45 - 7.2 (m, 5 H); 4.1 (s, 1 H); 3.5 (s, 3 H); 3.1 (s, 6 H); 1.6 (s, 3 H). ^{13}C-nmr δ 141.5, 127.9, 127.5, 127.2, 111.1, 81.9, 58.0, 57.35, 50.1, 15.6. Mass, m/e 195 (1), 179 (4), 135 (23), 105 (13), 75 (100). Found: C = 68.58, H = 8.59%. Requires: C = 68.55, H = 8.63%.

1,1,2-Trimethoxy-2,3-diphenyl propane, 28 (27%), oil. H-nmr δ 7.45 - 7.15 (m, 10 H); 4.15 (s, 1 H); 3.5 (s, 3 H); 3.45 (d, 1 H, J = 14.4 Hz); 3.35 (s, 3 H); 3.3 (s, 3 H); 3.25 (d, 1 H, J = 14.4 Hz). ^{13}C-nmr δ 137.1, 130.7, 128.4, 127.7, 127.4, 127.0, 126.0, 108.9, 84.0, 58.5, 56.5, 51.6, 38.8. Mass, m/e 255 (1), 195 (10), 121 (27), 105 (19), 75 (100). Found: C = 75.57, H = 7.72%. Requires: C = 75.50, H = 7.74%.

Synthesis of 1,3-diphenyl-1,3-dimethoxy propanes, 25.

To a solution of dibenzoylmethane (5 mmol) in ethanol (15 ml) $NaBH_4$ (8 mmol) was added and the mixture was stirred at room temperature for 15 h. The residue obtained after the usual work up was a mixture of the two **1,3-diphenyl-1,3-dihydroxy propanes**[30] (68%). H-nmr δ 7.25 (s, 5 H), 4.95 - 4.75 (m, 1 H); 3.6 (s, 1 H); 2.3 - 1.7 (m, 1 H). ^{13}C-nmr δ 144.2, 128.4, 127.5, 127.2, 125.7, 125.6, 74.6, 71.4, 47.5, 46.6.

The diols (1.42 g) were dissolved in DMF and treated with sodium hydride (0.45 g) at room temperature. Methyl iodide was then added and the mixture was stirred for 5 h. The residue obtained after the usual work up was chromatographed through a silica gel column using a mixture of benzene and ethyl acetate (98/2) as eluant. The following products were isolated:[31]

1,3-diphenyl-1,3-dimethoxy propane, 25, (40%), m.p. 62 - 64 °C. H-nmr δ 7.3 (s, 5 H); 4.45 (dd, 1 H, J = 6.0 and 7.5 Hz); 3.25 (s, 3 H); 2.0 (dd, 1 H, J = 6.0 and 7.5 Hz). ^{13}C-nmr δ 142.4, 128.4, 127.5, 126.6, 80.2, 56.8, 47.7. Mass, m/e 224 (20), 192 (5), 121 (100), 91 (22), 77 (37).

1,3-diphenyl-1,3-dimethoxy propane, (25%), oil. H-nmr δ 7.3 (s, 10 H); 4.05 (dd, 2 H, J = 6.6 and 7.5 Hz); 3.2 (s, 6 H); 2.5 (dt, 1 H, J = 7.5 and 13.2 Hz); 1.85 (dt, 1 H, J = 6.6 and 13.2 Hz). ^{13}C-nmr δ 141.8, 128.4, 127.6, 126.8, 80.9, 56.2, 46.3. Mass, m/e 224 (15), 192 (3), 121 (100), 91 (22), 77 (36).

1,3-diphenyl-1-methoxy-3-hydroxy propane, (15%) oil. H-nmr δ 7.5 - 7.1 (m, 10 H); 4.9 (dd, 1 H, J = 3.6 and 9.6 Hz); 4.4 (dd, 1 H, J = 3.6 and 9.6 Hz); 3.9br (s, 1 H); 3.25 (s, 3 H); 2.2 (dt, 1 H, J = 9.6 and 14.7 Hz); 1.85 (dt, 1 H, J = 3.6 and 14.7 Hz). ^{13}C-nmr δ 144.8, 144.4, 141.6, 141.3, 128.5, 128.3, 127.9, 127.3, 126.5, 126.45, 125.8, 125.6, 84.1, 81.1, 73.6, 71.0, 56.6, 56.3, 47.7, 46.9.

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