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ON THE REACTION OF TRISUBSTITUTED OLEFINS WITH PHENYLSELENENYL CHLORIDE IN METHANOL

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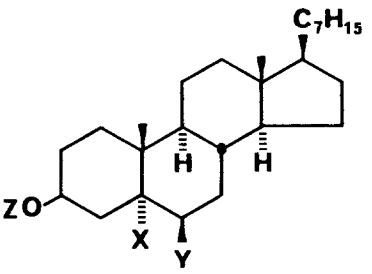
Summary: The interaction of trisubstituted olefins with excess phenylselenenyl chloride in methanol generates chloromethoxy and dimethoxyderivatives. The mechanism of this transformation has been investigated.

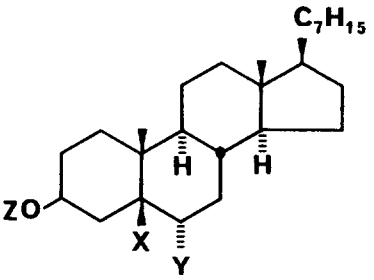
Phenylselenenyl chloride is known to react with olefins to produce, in an anti-stereospecific fashion, the β-chloro-,[1] β-hydroxy-,[2] or β-methoxy-selenides[3] depending on the reaction conditions. The removal of the selenium containing moiety from these adducts can be achieved, inter alia,[4] by transforming the selenides into selenonium salts with electrophilic reagents such as halogens or phenylselenenyl halides. By this procedure, the β-chloro and β-hydroxy-selenides have been transformed into cis-dichloro derivatives[5] and trans-halohydrins[6] respectively. Trans-halohydrins have been obtained in higher yields treating olefins with excess phenylselenenyl chloride; this procedure is particularly effective when the adduct is constrained to maintain the original anti-relationship.[6]

On the basis of these results we treated cholesterol with excess phenylselenenyl chloride in methanol (for 2 h) for the selective preparation of the corresponding trans chloromethoxy-derivative **1b**. The reaction, unexpectedly, produced a mixture of products, separated by column chromatography.[7] The adduct **1a** was isolated in a 62% yield, the

other components, **1b** (9%), **1c** (6%), **2a** (2%) and **2b** (4%) arise from the deselenylation process of **1a**. By extending the time (1 day), the reaction produced only the compounds **1b** (27%), **1c** (17%), **2a** (7%), and **2b** (12%). The structures of compounds 1 and 2 were clearly assigned from their spectral data.

The A/B trans (1) or cis ring junction (2) was proven by the ^{13}C NMR chemical shift value of the methyl group at C(10): in the cis isomers this carbon is deshielded vis-a-vis trans isomers, by removal of the γ effect on C(2) and C(4)[8]. Of special significance is the splitting pattern shown by the C(3)-H signal of compounds **2** (m, W 1/2 = 8 Hz) from which an equatorial orientation of C(3) hydrogen and hence a cis ring junction of A/B rings can be assigned. To facilitate the spectroscopic ^{1}H and ^{13}C attributions, compounds 1 and 2 were transformed into the corresponding acetates (**1d**, **1e**, **2c** and **2d**).



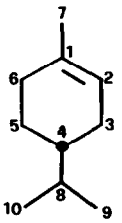


1a	X=OMe,	Y=SePh,	Z=H
1b	X=OMe,	Y=Cl,	Z=H
1c	X=OMe,	Y=OMe,	Z=H
1d	X=OMe,	Y=Cl,	Z=Ac
1e	X=OMe,	Y=OMe,	Z=Ac
1f	X=OMe,	Y=OCD_3,	Z=H

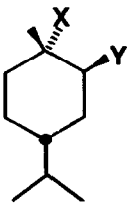
2a	X=Cl,	Y=OMe,	Z=H
2b	X=OMe,	Y=OMe,	Z=H
2c	X=Cl,	Y=OMe,	Z=Ac
2d	X=OMe,	Y=OMe,	Z=Ac
2e	X=OCD_3,	Y=OMe,	Z=H

In order to explore the methoxyselenenylation-deselenenylation process in simpler models, the p-menthene 3 was treated with excess phenylselenenyl

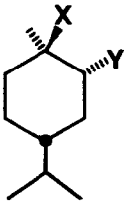
chloride for 2 h. Under these conditions 3 gave the chlorometoxy- **4b** (8%), 5a (8%), dimetoxy-derivatives **4c** (12%), **5b** (41%) and only small amount of the adduct **4a** (5%).



3a

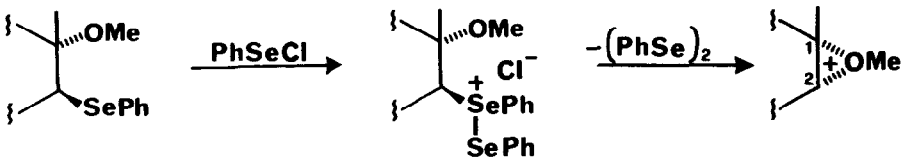


4a X=OMe, Y=SePh
4b X=OMe, Y=Cl
4c X=OMe, Y=OMe



5a X=Cl, Y=OMe
5b X=OMe, Y=OMe

The observed regio- and stereo-chemistry in the deselenenylation process of adduct a is presumably due to the participation of the neighbouring methoxy group in the displacement of the selenonium chloride b, which generates the oxonium ion c (Scheme). The intermediate c can interact with a nucleophile at both bridge carbons.



a **b** **c**

In the opening of c the methanol competes with the chloride ion. Thus the dimethoxyderivatives **1c**, **2b**, **4c** and **5b** were obtained in addition to the expected chloromethoxyderivatives **1b** and **4b**.

In the formation of **2a** and **2b** for example, the methoxy group of **1a** must transpose stereospecifically. Evidence for such a proposed mechanism comes from the interaction of **1a** with excess PhSeCl in methanol-d_4; under these conditions **1b**, **2a** and the deutero-compounds **1f** and **2e** are formed. The ^{13}C and ^{1}H NMR analysis reveals in **1f** and **2e** the presence of a deuteromethoxy group at C(6) and C(5) respectively.

EXPERIMENTAL

Melting points were obtained on a Reichert micro hotstage and are uncorrected. ^{1}H NMR spectra were recorded at 90 MHz on a Varian EM390 instrument in $CDCl_3$ solution using TMS as reference. ^{13}C NMR spectra were recorded at 20.15 MHz on a Bruker WP80SY instrument, in the Fourier transform mode with proton decoupling throughout, in $CDCl_3$ solutions using TMS as reference. Elemental analyses were carried out on a Carlo Erba Model 1106 Elemental Analyzer. Column chromatography was carried out on 0.063-0.200 mesh Merck silica gel. All extracts were dried over Na_2SO_4.

Reaction of cholesterol with PhSeCl.(2 hr) 2.3 g of phenylselenenyl chloride (12 mmol) were added to a stirring solution of 1.16 g of cholesterol (3 mmol) in 60 ml of methanol. The reaction mixture was stirred at room temperature for 2 hours and then poured into 200 ml of water, neutralized with sodium bicarbonate and extracted with chloroform. The combined organic layers were washed with water, dried and evaporated. Medium pressure coloumn chromatography (SiO_2/Benzene: ethyl acetate =

24:1) gave: **2a** (0.025 g, 2%), ^{1}H NMR δ 3.49 (s, 3, OMe), 3.51 (dd, J = 3 Hz and J = 9 Hz, H-6), 4.09 (m, 1, H-3), ^{13}C NMR δ 11.9 (C-18), 18.6 (C-21), 19.5 (C-19), 22.1 (C-11), 22.5 (C-26), 22.7 (C-27), 23.8 (C-15), 24.1 (C-23), 25.9 (C-7), 27.2 (C-2), 28.0 (C-25), 28.1 (C-16), 33.2 (C-8), 33.5 (C-4), 34.5 (C-1), 35.7 (C-20), 36.1 (C-22), 39.5 (C-24), 39.8 (C-12), 42.5 (C-9), 42.8 (C-13), 42.9 (C-10), 56.1 (C-14), 56.3 (C-17), 58.6 (6-OCH_3), 65.9 (C-3), 83.7 (C-6), 85.9 (C-5). Anal. Calcd. for $C_{28}H_{49}ClO_2$: C, 74.21; H, 10.89. Found: C, 73.98; H, 10.92; **1a** (1.1 g, 62%). ^{1}H NMR δ 3.07 (s, 3, OMe), 3.36 (m, 1, H-6), 3.73 (m, 1, H-3), 7.2-7.7 (m, 5, aromatic protons), ^{13}C NMR δ 12.2 (C-18), 18.0 (C-19), 18.6 (C-21), 21.2 (C-11), 22.5 (C-26), 22.7 (C-27), 23.8 (C-15), 24.2 (C-23), 27.9 (C-25), 28.2 (C-16), 31.1 (C-2), 31.1 (C-8), 32.2 (C-1), 34.3 (C-4), 35.8 (C-20), 36.2 (C-22), 36.8 (C-7), 39.5 (C-24), 40.0 (C-12), 40.4 (C-10), 42.8 (C-13), 44.9 (C-9), 47.0, (5-OCH_3), 47.7 (C-6), 55.5 (C-14), 56.3 (C-17), 67.7 (C-3), 81.1 (C-5). Anal. Calcd. for $C_{34}H_{58}O_2Se$: C, 70.67; H, 10.11. Found: C, 70.48; H, 10.21; **1b** (0.12 g, 9%), m.p. 155-156 °C, ^{1}H NMR δ 3.13 (s, 3, OMe), 3.73 (m, 1, H-3), 4.13 (m, 1, H-6), ^{13}C NMR δ 12.1 (C-18), 18.6 (C-21), 19.0 (C-19), 21.1 (C-11), 22.5 (C-26), 22.8 (C-27), 23.8 (C-15), 24.1 (C-23), 28.0 (C-25), 28.2 (C-16), 29.9 (C-8), 31.0 (C-2), 32.6 (C-1), 34.6 (C-4), 35.6 (C-7), 35.8 (C-20), 36.2 (C-22), 39.5 (C-24), 40.0 (C-12), 40.2 (C-10), 42.8 (C-13), 44.6 (C-9), 47.9 (5-OCH_3), 55.4 (C-14), 56.3 (C-17), 58.9 (C-6), 67.4 (C-3), 79.9 (C-5). Anal. Calcd. for $C_{28}H_{49}ClO_2$: C, 74.21; H, 10.89. Found: C, 74.01; H, 10.98; **2b** (0.05 g, 4%), ^{1}H NMR δ 3.30 (s, 3, C-6 OMe), 3.43 (dd, J = 6 Hz and J = 9 Hz, H-6), 3.48 (s, 3, C-5 OMe), 3.94 (m, 1, H-3), ^{13}C NMR δ 11.9 (C-18), 17.4 (C-19), 18.6 (C-21), 21.2 (C-11), 22.5 (C-26), 22.7 (C-27), 23.8 (C-15), 24.0 (C-23), 25.4 (C-7), 27.0 (C-4), 27.7 (C-2), 28.0 (C-25), 28.2 (C-16), 33.1 (C-1), 35.7 (C-8), 35.7 (C-20), 36.2 (C-22), 39.5 (C-24), 39.8 (C-12), 42.3 (C-10), 42.6 (C-13), 42.9 (C-9), 52.9 (5-OCH_3), 55.0 (6-OCH_3), 56.3 (C-14), 56.5 (C-17), 66.7 (C-3), 79.5 (C-6), 82.2 (C-5). Anal. Calcd.

for $C_{29}H_{52}O_3$: C, 77.62; H, 11.68. Found: C, 77.81; H, 11.52; **1c** (0.07 g, 6%), ^{1}H NMR δ 3.16 (s, 3, C-5 OMe), 3.23 (m, 1, H-6), 3.30 (s, 3, C-6 OMe), 3.73 (m, 1, H-3). ^{13}C NMR δ 12.2 (C-18), 17.0 (C-19), 18.7 (C-21), 21.1 (C-11), 22.5 (C-26), 22.7 (C-27), 23.9 (C-15), 24.2 (C-23), 28.0 (C-25), 28.3 (C-16), 29.1 (C-7), 30.4 (C-8), 31.3 (C-2), 31.9 (C-1), 33.7 (C-4), 35.8 (C-20), 36.2 (C-22), 39.5 (C-24), 39.6 (C-10), 40.1 (C-12), 42.8 (C-13), 44.8 (C-9), 47.9 (5-OCH_3), 56.0 (C-14), 56.3 (C-17), 57.9 (6-OCH_3), 67.7 (C-3), 79.2 (C-5), 79.6 (C-6). Anal. Calcd for $C_{29}H_{52}O_3$: C, 77.62; H, 11.68. Found: C, 77.49; H, 11.75.

Reaction of cholesterol with PhSeCl (24 h). 2.3 g of phenylselenenyl chloride (12 mmol) were added to a stirring solution of 1.16 g of cholesterol (3 mmol) in 60 ml of methanol. The reaction mixture was stirred at room temperature for 24 h. Workup as above afforded **2a** (0.09 g, 7%), **1b** (0.36 g, 27%),**2b** (0.16 g, 12 %) and **1c** (0.23 g, 17%).

Reaction of 1a with PhSeCl in CD_3OD. 0.57 g. of phenylselenenyl chloride (3 mmol) were added to a stirring solution of 0.57 g. of **1a** (1 mmol) in 10 ml of CD_3OD. The reaction mixture was stirred at room temperature for 24 h. Workup as above afforded: **2a** (0.04 g, 9%), **1b** (0.12 g, 29%), **2e** (0.06 g, 13%),^{1}H NMR δ 3.30 (s, 3, C-6, OMe), 3.43 (dd, J = 3 Hz and J = 9 Hz, 1, H-6), 3.93 (m, 1, H-3), ^{13}C NMR δ 11.9 (C-18), 17.4 (C-19), 18.6 (C-21), 21.1 (C-11), 22.5 (C-26), 22.7 (C-27), 23.8 (C-15), 24.2 (C-23), 25.4 (C-7), 27.0 (C-4), 27.7 (C-2), 27.9 (C-25), 28.1 (C-16), 33.1 (C-1), 35.7 (C-8), 35.7 (C-20), 36.1 (C-22), 39.5 (C-24), 39.8 (C-12), 42.2 (C-10), 42.5 (C-13), 42.8 (C-9), 52.1 (5-OCD_3, seven lines), 55.0 (6-OCH_3), 56.1 (C-14), 56.5 (C-17), 66.6 (C-3), 79.5 (C-6), 82.0 (C-5). **1f** (0.08 g., 18%) ^{1}H NMR δ 3.16 (s, 3, C-5 OMe), 3.23 (m, 1, H-6), 3.76 (m, 1, H-3), ^{13}C NMR 12.1 (C-18), 17.0 (C-19), 18.6 (C-21), 21.1 (C-11), 22.5 (C-26), 22.7 (C-27), 23.8 (C-15), 24.2 (C-23), 28.0 (C-25), 28.2 (C-16), 29.0 (C-7), 30.3

(C-8), 31.2 (C-2), 31.9 (C-1), 33.7 (C-4), 35.8 (C-20), 36.2 (C-22), 39.5 (C-24), 39.9 (C-10), 40.1 (C-12), 42.8 (C-13), 44.8 (C-9), 48.7 (6-OCD_3, seven lines), 56.0 (C-14), 56.3 (C-17), 57.1 (5-OCH_3), 67.7 (C-3), 79.2 (C-5), 79.5 (C-6).

General procedure for the acetylation of alcools 1b, 1c, 2a, and 2b. A solution of alcohols (0.5 mmol) and 1 ml of acetic anhydride in 3 ml of pyridine was kept at room temperature for 12 h. The solution was poured into 10 ml of water, neutralized with sodium bicarbonate and extracted with chloroform. The organic layer was washed with water, dried and evaporated. The crude products were chromatographed ($SiO_2/CHCl_3$); spectral data of compounds are reported below.

Acetate 1d, (93%), ^1H NMR δ 2.0 (s, 3, OAc), 3.20 (s, 3, OMe), 4.11 (m, 1, H-6), 4.47 (m, 1, H-3), ^{13}C NMR δ 12.1 (C-18), 18.6 (C-21), 18.9 (C-19), 21.0 (C-11), 21.2 ($OCO\underline{C}H_3$), 22.5 (C-26), 22.7 (C-27), 23.8 (C-15), 24.1 (C-23), 26.5 (C-2), 27.9 (C-25), 28.2 (C-16), 29.9 (C-8),30.9 (C-4), 32.3 (C-1), 35.3 (C-7), 35.7 (C-20), 35.7 (C-22), 39.5 (C-24), 39.9 (C-12), 40.3 (C-10), 42.7 (C-13), 44.5 (C-9), 48.2 (5-OCH_3), 55.3 (C-14), 56.3 (C-17), 58.7 (C-6), 70.7 (C-3), 79.6 (C-5), 172.4 (C=0).

Acetate 1e, (90%), ^1H NMR δ 2.0 (s, 3, OAc), 3.15 (s, 3, OMe), 3.20 (s, 3, OMe), 3.18 (m, 1, H-6), 4.76 (m, 1, H-3), ^{13}C NMR δ 12.1 (C-18), 16.9 (C-19), 18.7 (C-21), 21.0 (C-11), 21.4 ($OCO\underline{C}H_3$), 22.5 (C-26), 22.8 (C-27), 23.9 (C-15), 24.2 (C-23), 26.7 (C-2), 28.0 (C-25), 28.3 (C-16), 28.9 (C-7), 29.9 (C-4), 30.3 (C-8), 31.6 (C-1), 35.8 (C-20), 36.2 (C-22), 39.5 (C-24), 39.7 (C-10), 40.0 (C-12), 42.8 (C-13), 44.8 (C-9), 48.2 (5-OCH_3), 55.9 (C-14), 56.3 (C-17), 57.7 (6-OCH_3), 71.2 (C-3), 79.0 (C-5), 79.5 (C-6), 170.8 (C=0).

Acetate 2c, (88%), ^{1}H NMR δ 2.04 (s, 3, OAc), 3.45 (s, 3, OMe), 3.48 (dd, J = 3 and J = 9, 1, H-6), 5.1 (m, 1, H-3), ^{13}C NMR δ 11.9 (C-18), 18.6 (C-21), 19.3 (C-19), 21.6 ($OCO\underline{C}H_3$), 22.0 (C-11), 22.5 (C-26), 22.7 (C-27), 23.8 (C-15), 24.1 (C-23), 24.1 (C-2), 26.6 (C-7), 27.9 (C-25), 28.1 (C-16), 31.3 (C-4), 33.3 (C-8), 34.3 (C-1), 35.7 (C-20), 36.1 (C-22), 39.5 (C-24), 39.8 (C-12), 42.4 (C-10), 42.5 (C-13), 42.8 (C-9), 56.1 (C-14), 56.3 (C-17), 58.6 (6-OCH_3), 67.6 (C-3), 81.5 (C-5), 83.8 (C-6), 170.6 (C=O).

Acetate 2d, (86%), ^{1}H NMR δ 1.92 (s, 3, OAc), 3.14 (s, 3, Ome), 3.20 (m, 1. H-6), 3.27 (s, 3, OMe), 4.94 (m, 1, H-3), ^{13}C NMR δ 11.9 (C-18), 17.3 (C-19), 18.6 (C-21), 21.0 (C-11), 21.4 ($OCO\underline{C}H_3$), 22.5 (C-26), 22.6 (C-4), 22.7 (C-27), 23.8 (C-15), 24.2 (C-23), 24.5 (C-2), 25.9 (C-7), 28.0 (C-25), 28.1 (C-16), 33.1 (C-8), 33.8 (C-1), 35.7 (C-20), 36.1 (C-22), 39.5 (C-24), 39.9 (C-12), 41.5 (C-10), 42.5 (C-13), 42.7 (C-9), 52.4 (5-OCH_3), 55.5 (6-OCH_3), 56.1 (C-14), 56.6 (C-17), 68.8 (C-3), 77.9 (C-5), 83.9 (C-6), 170.7 (C=O).

Reaction of p-menth-1-ene with PhSeCl. 3.5 g of phenylselenenyl chloride (18 mmol) were added to a stirring solution of 0.5g of p-menth-1-ene (3.6 mmol) in 50 ml of methanol. The reaction mixture was stirred at room temperature for 2 h and then poured into 200 ml of water, neutralized with sodium bicarbonate and extracted with chloroform.The combined organic layers were washed with water, dried and evaporated. Medium pressure column chromatography (SiO_2 petrolium ether: ethyl acetate=20:1) gave **5a** (0.060 g, 8%), ^{1}H NMR δ 0.88 (d, J = 6.5 Hz, 6, H_3-9 and H_3-10), 1.51 (s, 3, H_3-7), 3.32 (dd, J = 11.5 and 5, 1, H-2), 3.52 (s, 3, OMe), ^{13}C NMR δ 17.7 (C-9 and C-10), 21.5 (C-7), 26.6 (C-5), 32.0 (C-3), 32.1 (C-8), 42.3 (C-4), 42.4 (C-6), 58.4 (OMe), 73.9 (C-1), 86.9 (C-2). Anal. Calcd. for $C_{11}H_{21}ClO$: C, 64.53; H, 10.34. Found: C, 64.41; H, 10.48; **4b** (0.06 g, 8%),

^{1}H NMR δ 0.88 (d, J = 6.5 Hz, 6, H_3-9 and H_3-10), 1.25 (s, 3, H_3-7), 3.20 (s, 3, OMe), 4.09 (m, 1, H-2); ^{13}C NMR δ 19.8 (C-9 and C-10), 21.9 (C-7), 23.9 (C-5), 29.3 (C-6), 31.% (C-8), 33.2 (C-3), 36.0 (C-3), 48.9 (O-Me), 64.2 (C-2), 75.7 (C-1); Anal. Calcd. for $C_{11}H_{21}ClO$: C, 64.53; H, 10.34. Found: C, 64.38; H, 10.51. **4a**(0.01 g%); ^{1}H NMR δ 0.82 and 0.87 (each d, J = 6.5 Hz, 6, H_3-9 and H_3-10), 3.18 (s, 3, O-Me), 3.59 (m, 1, H-2); ^{13}C NMR δ 19.9 (C-9 and C-10), 23.6 (C-7), 24.4 (C-5), 31.7 (C-6), 32.2 (C-8), 32.6 (C-3), 38.6 (C-5), 48.6 (OMe), 52.1 (C-2), 76.3 (C-1), 127.2, 129.0, 131.2, 134.1 (aromatic carbons); Anal. Calcd. for $C_{17}H_{26}OSe$: C, 62.76; H, 8.05. Found: C, 62.87; H, 7.95; **4c** (0.09 g, 12%), ^{1}H NMR δ 0.77 and o.83 (each d, J = 6.5 Hz, 6, H_3-9 and H_3-10), 1.06 (s, 3, H_3-7), 3.09 (s, 3, OMe), 3.23 (s, 3, OMe), 3.02 (m, 1, H-2); ^{13}C NMR δ 20.6 (C-7), 19.7, 19.8 (C-9 and C-10), 24.1 (C-5), 27.0 (C-2), 29.9 (C-6), 32.3 (C-8), 36.3 (C-4), 48.1 (1-OMe), 56.9 (2-OMe), 75.2 (C-1), 81.9 (C-2); Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.79; H, 12.21; **5b** (0.3 g, 41%), ^{1}H NMR δ 0.85 (d, J = 6.5 Hz, 6, H_3-9 and H_3-10), 1.12 (s, 3, H_3-7), 3.15 (dd, J = 5 and 11 Hz, 1, H-2), 3.25 (s, 3, OMe), 3.40 (s, 3, OMe9, ^{13}C NMR δ 14.9 (c-7), 19.6 (C-9 and C-10), 25.9 (C-5), 31.3 (C-3), 32.1 (C-8), 34.4 (C-6), 49.0 (1-OMe), 57.4 (2-OMe), 77.7 (C-1), 84.2 (C-2); Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.10; H, 11.93.

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