# Steroidal Selenoxides Diastereoisomeric at Selenium; *syn*-Elimination, Absolute Configuration, and Optical Rotatory Dispersion Characteristics

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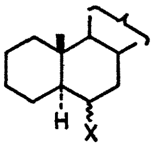
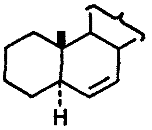
*Summary* Steroidal selenoxides have been separated chromatographically into diastereoisomers at selenium, and their mode of elimination permitted allocations of configuration at selenium; their chiroptical properties were similar to those of related sulphoxides.

SELENOXIDES have a pyramidal configuration at selenium according to n.m.r.[1] and mixed crystal studies,[2] but attempts to resolve dissymmetric selenoxides have failed.[3] This failure, which contrasts with the ease of resolution of the related sulphoxides[4] and selenonium salts,[3b,5] has been attributed to fast racemization *via* an intermediate hydrate achiral at selenium.[1,6] We have used steroidal systems, which were successful for sulphoxides,[7] to separate selenoxides diastereoisomeric at selenium for the first time, and to investigate their chirality.

6α-Methanesulphonyloxy-5α-cholestane (Ia) with sodium benzeneselenolate (PhSeNa) gave the 6β-phenylselenide (Ib), which was oxidised by ozone in dichloromethane at −78° (conditions that convert selenides into selenoxides but not into selenones)[8] to give a mixture of the (*R*)- and (*S*)-6β-phenylselenoxides (Ic and Id) in the ratio 2:1. These gave well-separated discrete spots on t.l.c. on silica at 0°, and were separated on a preparative scale by chromatography on a column of alumina at −50°. T.l.c. examination showed that the selenoxides did not interconvert perceptibly at temperatures between −78° and 25° in hexane, chloroform, or ether, either in the absence or presence of water. Pyramidal inversion, or racemization *via* reversible hydrate formation is therefore not important for the selenoxides (Ic) and (Id) under these conditions.


(I)

a X = 6α-$MeSO_2$·O
b X = 6β-PhSe
c X = (*R*)-6β-PhSeO
d X = (*S*)-6β-PhSeO
e X = (*R*)-6β-PhSO
f X = (*S*)-6β-PhSO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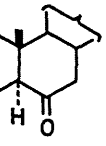

(III)

Both selenoxides (Ic) and (Id) decomposed rapidly in hexane at room temperature to give only (>95%) 5α-cholest-6-ene (II) and benzeneseleninic acid ($PhSeO_2H$), but whereas one isomer decomposed completely to the olefin (II) after 4 hr. at 0°, the other was inert under these conditions. The absence of detectable quantities of 5α-cholestan-6-one (III) as a decomposition product indicated that rearrangement to a selenenate[6] or α-hydroxy-selenide,[9] previously invoked to explain the thermal instability of alkyl selenoxides, does not apply for (Ic) and (Id), and the formation of only 5α-cholest-6-ene (II) (and no cholest-5-ene) suggested *syn*-elimination, a reaction not previously reported for selenoxides although known for sulphoxides.[10]

The difference in rates of decomposition of the diastereoisomeric selenoxides (Ic) and (Id) at 0° is rational in terms of the cyclic intramolecular mechanism usually associated with *syn*-eliminations,[11] since of the two transition states required by this mechanism which lead from the (*R*)- and (*S*)-6β-phenylselenoxides to 5α-cholest-6-ene, the one (A) from the (*S*)-isomer (Id) is appreciably less sterically compressed than that (B) from the (*R*)-isomer (Ic). Since the energy difference between the (*R*)- and (*S*)- selenoxides is small, this interpretation leads to an allocation of (*S*)-configuration at selenium to the more reactive selenoxide.

The o.r.d. curves of the selenoxides (Figure) are similar in sign and position to those of the corresponding (*R*)- and (*S*)-6β-phenylsulphoxides (Ie and If) the configurations at sulphur of which were also established by the pyrolytic method, the (*S*)-sulphoxide (If) decomposing to 5α-cholest-6-ene (II) under conditions (100° in toluene) where the (*R*)-isomer was almost inert. The considerably faster decomposition of the selenoxides than sulphoxides may be

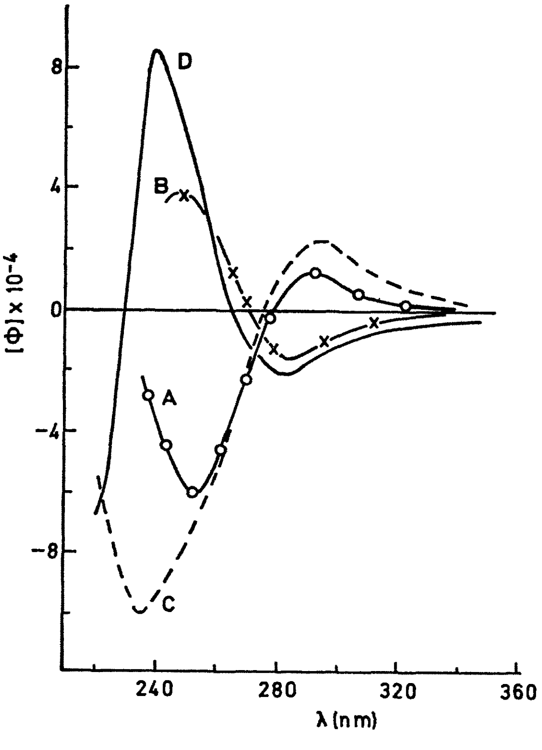
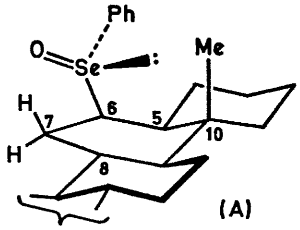


FIGURE. *O.r.d. curves of* 6β-*phenylseleninyl- and* 6β-*phenylsulphinyl*-5α-*cholestanes in hexane.*
[A = (Ic), B = (Id), C = (Ie), D = (If).]

associated with the greater basicity of the oxygen in selenoxides than sulphoxides,[3a] which should facilitate intramolecular removal of a $\beta$-proton.

Further points of similarity between the selenoxides (Ic and Id) and the sulphoxides (Ie and If) include the occurrence of the u.v. maxima at higher wavelengths in the (*R*)- than (*S*)-isomers [(Ic) $\lambda_{\max}$ 265 nm, $\epsilon$ 3000, (Id) $\lambda_{\max}$ 245 nm, $\epsilon$ 4200, (Ie) $\lambda_{\max}$ 272 nm, $\epsilon$ 2750, (If) $\lambda_{\max}$ 261, $\epsilon$ 4700], the increased ratio of (*R*)- to (*S*)-isomers obtained when hexane was used instead of dichloromethane in the oxidation of the 6$\beta$-selenide or 6$\beta$-sulphide by ozone, and the greater mobility of the (*S*)-isomers on t.l.c. (silica). Similar correlations of chiroptical, spectroscopic, and chemical properties were found between steroidal (*R*)- and (*S*)-6$\beta$-benzylselenoxides and (*R*)- and (*S*)-benzylsulphoxides, and between (*R*)- and (*S*)-4$\beta$-phenylselenoxides and their sulphur analogues, suggesting that comparison of these properties of selenoxides with those of related sulphoxides of known chirality may subsequently be used to allocate configuration at selenium.



(A)

[B; as (A), with Ph and lone pair interchanged]

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