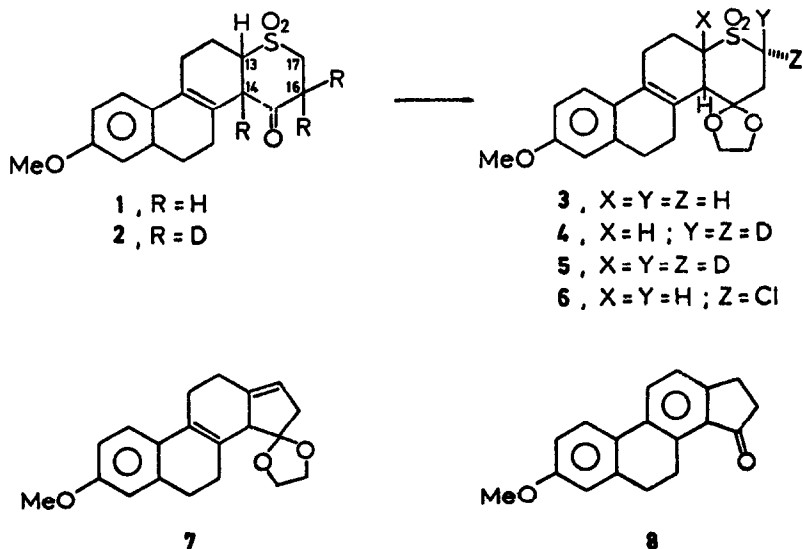


BASE INDUCED REARRANGEMENT OF TETRACYCLIC α -HALOSULFONES.
RAMBERG BÄCKLUND SYNTHESIS OF A STEROIDAL SKELETON
AND ITS STRUCTURAL ELUCIDATION.

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Several Diels-Alder reactions of 1,3-dienes with 2,3-dihydrothiopyran-4-one¹ S,S-dioxide and its derivatives have been reported in the literature.² Some of these lead to thiapyranosteroids of ambiguous dienophile orientation.³ This communication describes (i) the synthesis of 1, (ii) a reliable method to establish the relative orientation of diene and dienophile and (iii) the conversion of 1 to 3-methoxy-15-ethylenedioxy-estra-1,3,5(10),8,13(17)-pentaene (7).



Reaction of 1-vinyl-6-methoxy-3,4-dihydronaphthalene⁴ with 2,3-dihydrothiopyran-4-one S,S-dioxide in benzene at 150° gave a crystalline mixture (mp 200-232°) from which 1 was isolated in 65% yield (mp 235-238°) after recrystallization from dioxane.

Conversion of 1 to its cyclic acetal 3 (mp 215-220°, EtOH, 63%) and metallation of 3 with n-butyllithium in benzene followed by chlorination with hexachloroethane⁵ afforded 6 (mp 188-191°, EtOH/CHCl₃, 41%).

Treatment of the α-halosulfone 6 with KOtBu in DME⁶ gave complete conversion to the desulfurised β,γ-unsaturated acetal 7, isolated as a colourless liquid. NMR (CDCl₃): 7.08 (C₁-H, d, J_{1,2} 9Hz), 6.7 (C₂- and C₄-H, m), 5.42 (C₁₇-H, m, W_{1/2} 6Hz), 3.9 (acetal, s), 3.76 (OCH₃, s), 3.38 (C₁₄-H, narrow m, W_{1/2} 3Hz), 2.8-2.2 (remaining 10H).

Acid catalysed hydrolysis of 7 led to a mixture from which 8⁷ was isolated by chromatographic separation (mp 158-160°, 50%). UV^{EtOH}_{max}: 215 (26820), 260 (20454), 283 (18636); m/e 264; IR (KBr): 1695, 1605, 1470 and 1240 cm⁻¹; NMR (CDCl₃): 7.85 (C₁₁-H, J_{11,12} 8Hz), 6.82 (C₂- and C₄-H, m), 3.82 (OCH₃, s), 3.40 (C₁₇-H, m), 3.08 (C₁₆-H, m), 2.9-2.6 (remaining H). Compound 8 presumably originates from a disproportionation of the initially formed pentaene.

It is not possible to locate the C₁₃- and C₁₄-H signals in the NMR spectra of 1 or 3 with certainty. Consequently neither the relative orientation of diene and dienophile nor the mode of C/D ring fusion can be established. However, acid catalyzed H/D exchange of all three enolisable hydrogens α to the carbonyl function in 1, yielding 2, and base catalyzed exchange of two or three hydrogens α to the SO₂ group in 3; leading to 4 and 5⁸, respectively, enabled us to detect the location of the NMR signals produced by the various hydrogens.

C₁₄-H in 1 (100 MHz, CDCl₃) at δ 3.90 (d, J_{13,14} 5Hz) is clearly allylic and incompatible with an alternative structure in which SO₂ and C=O have been interchanged. Moreover the J value reflects the C/D-cis ring

fusion. Comparison of the spectra of 3, 4 and 5 gives C_{14} -H (δ 3.26, $J_{13,14}$ 3.5Hz) and C_{13} -H (δ 3.02, $W_{\frac{1}{2}}$ 10Hz). These signals also confirm the dienophile orientation and C/D-cis ring fusion. The SO_2 group is in a position axial to ring C.

The structure of the monochlorinated sulfone 6, with equatorial Cl follows from the ABX-pattern formed by C_{16} - and C_{17} -H. C_{17} -H, δ 4.96 (x-part, $J_{AX} + J_{BX}$ 17 Hz). The C/D-cis ring fusion can be seen from $W_{\frac{1}{2}}$ (14Hz) of C_{13} -H at δ 3.40.

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7. In good agreement with a comparable compound described by Windholz e.a., *Tetrahedron Letters* 3331 (1967).
8. The reverse exchange yielding the starting materials, showed that no

change in stereochemistry had taken place, in either of these labeling experiments. The base catalysed exchange was performed at $p_H = 10$, 20 hr, 80° , as described by us, Recl. Trav. Chim. 94, 89 (1975). The double exchange proved completely geminal, as could be seen from the appearance of the C_{16} -H AB-pattern. Base catalysed exchange at $p_H = 11$ led to the D_3 -sulfone 5.