Elimination Reactions of *cis*- and *trans*-8a-Hydroxy-2-thiadecalin 2,2-Dioxide with Thionyl Chloride. Evidence for Intermediacy of Ion Pairs

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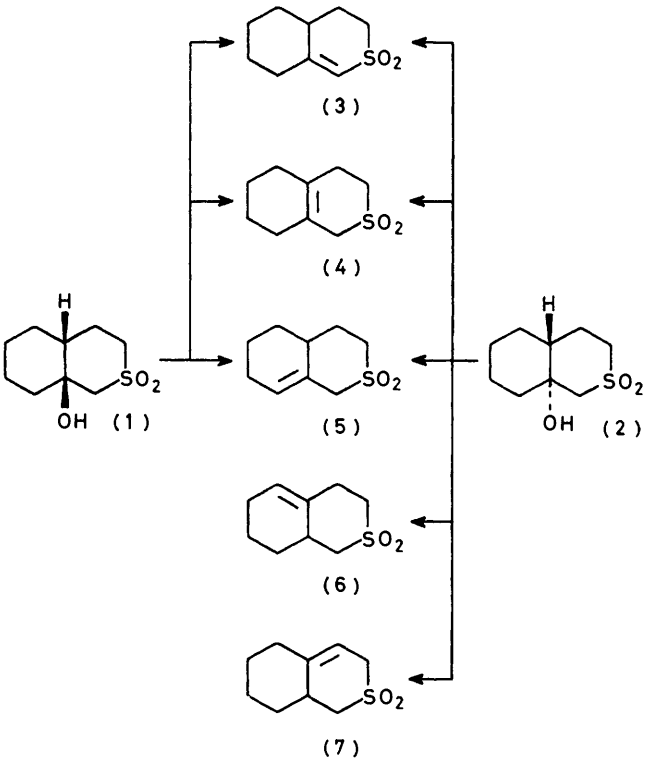
cis- and *trans*-8a-Hydroxy-2-thiadecalin 2,2-dioxide react with thionyl chloride to afford mixtures of unsaturated sulphones. The *cis*-isomer furnishes only the expected three isomeric olefins [$\Delta^{1(8a)}$, $\Delta^{4a(8a)}$, and $\Delta^{8(8a)}$], whereas the *trans*-isomer, besides the same unsaturated derivatives, also furnishes, unexpectedly, the isomeric $\Delta^{4a(5)}$- and $\Delta^{4(4a)}$-olefins. A mechanism involving the intermediacy of tight ion pairs is suggested.

We have previously reported the synthesis of *cis*- (1) and *trans*-8a-hydroxy-2-thiadecalin 2,2-dioxide (2).[1] In order to assess the reactivity of the angular hydroxy-group, both compounds were treated with thionyl chloride; in this way only mixtures of isomeric unsaturated sulphones were obtained; no chlorinated compounds were formed (Scheme 1).



Scheme 1

The *cis*-8a-hydroxy-sulphone (1) furnished, at room temperature or on heating, mixtures of the olefins (3)—(5) already described.[1] They were identified by g.l.c. analysis, but the isomer ratios could be calculated only by integration of the vinyl proton n.m.r. signals (Table 1). The presence of the tetrasubstituted olefin (4) was further confirmed by its conversion into the epoxide (8).[1]

The *trans*-8a-hydroxy-sulphone (2) reacted with thionyl chloride only on heating. Numerous attempts to analyse the reaction mixture by g.l.c. failed, owing to overlapping of various peaks, but n.m.r. spectroscopy was of some help in determining its composition. Of the three signals at δ 6.11, 5.80, and 5.40, the first corresponded to the vinylic proton of (3). The other two were thought to be due to isomeric olefins, *e.g.* (6) or (7), as was later confirmed. To solve this problem, we attempted independent syntheses of compounds (6) and (7) (Scheme 2).

Catalytic hydrogenation of the hydroxy-olefin (9),

Table 1

Distribution (%) of olefins in the reaction mixtures from the hydroxy-sulphones (1) and (2) with thionyl chloride, and chemical shifts of the vinylic protons

Hydroxy-sulphone	Temp.	Olefin	%	δ
(1)	Room temp.	(3)	0.5	6.11
		(4)	87.0	
		(5)	12.5	5.85
	79 °C	(3)	3.0	6.11
		(4)	69.0	
		(5)	28.0	5.85
(2)	Room temp.	No reaction		
	79 °C	(3)	7.0	6.11
		(4)	27.0	
		(5)	53.0	5.85
		(6)		5.80
		(7)	13.0	5.40

obtained from the epoxide (8) as previously reported,[1] led to a mixture of *trans*- (10) and *cis*- (11) 4a-hydroxy-sulphones. Their stereochemistry was defined by the results of pyrolysis of their acetyl derivatives. A stereospecific *cis*-elimination[2] takes place in this reaction, and as a consequence the structures of the products are established unambiguously.

The mixture of olefins (6) and (7) derived from the acetyl derivative of (10) displayed two ^{1}H n.m.r. peaks at δ 5.80 and 5.40 in the ratio 84 : 16. Attempted separation of the two products afforded a sample only of the former olefin (δ 5.80) which proved to be the isomer (6), identified by conversion into the epoxide (12) (Scheme 3). The remarkable stability of this epoxide in basic medium proved that the parent compound was (6) and not (7), since the latter, a βγ-unsaturated sulphone, would have given an epoxide rearranging immediately under basic conditions.[3] The stereochemistry of the epoxide (12) was demonstrated by its stereospecific reduction to (10).

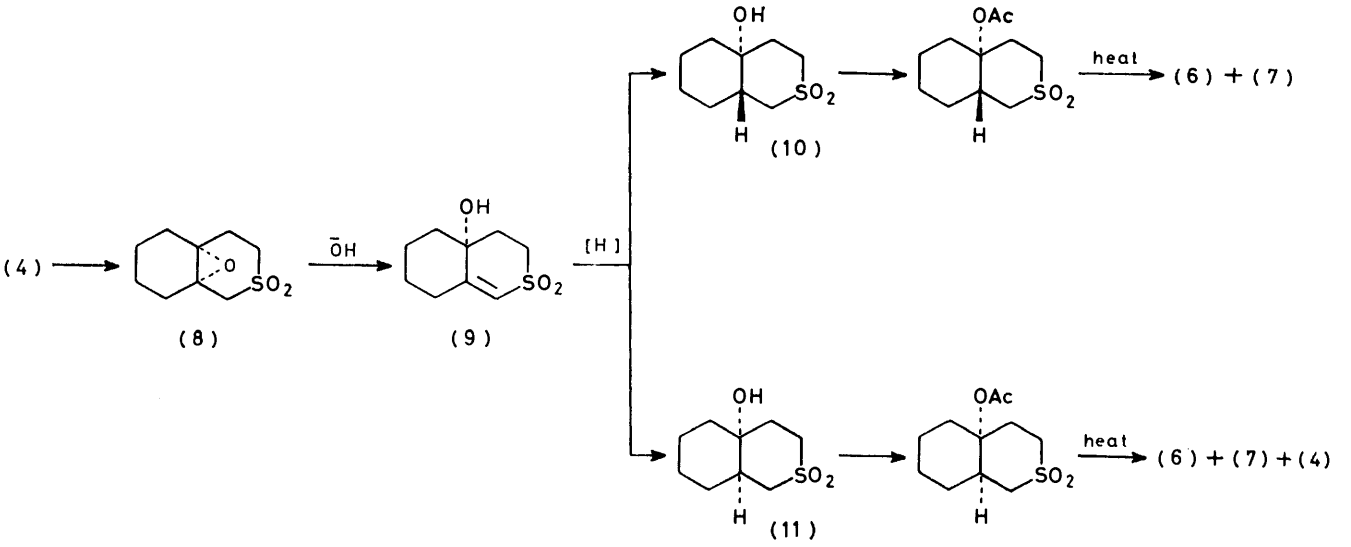
The question then arising was whether or not the

[1] S. Fabrissin, S. Fatutta, and A. Risaliti, *Gazzetta*, in the press.

[2] C. H. Depuy and R. W. King, *Chem. Rev.*, 1960, **60**, 431.

[3] A. Weissenberger, 'Heterocyclic Compounds with Three- and Four-membered Rings,' Part 1, Interscience, New York–London–Sidney, 1964, 266.

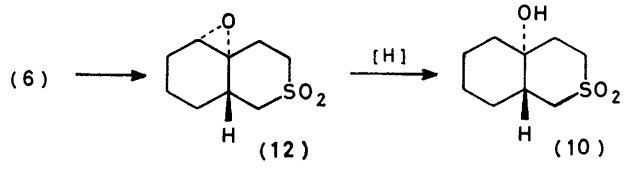
olefins (3), (6), and (7) were the only products of the reaction of the hydroxy-sulphone (2) with thionyl chloride. The crude reaction mixture was therefore epoxidized; and the epoxides of (4) and (5) were detected and isolated. Thus a signal at δ 5.85 due to the olefin (5) must have been hidden by the signal due to (6) (δ 5.80). Hence the *trans*-8a-hydroxy-sulphone (2) ever only (13), owing to the presence in the 4a-position of an axial hydrogen atom in the *trans*-configuration relative to the counter ion, can rearrange into the ion pair (15), more stable for steric reasons, which in turn can afford the olefins (6) and (7) through the corresponding carbocation. In contrast, analogous rearrangement of (14) into (16) would be impossible because



SCHEME 2

afforded a mixture of five isomeric unsaturated sulphones (Table 1).

It is reported[4] that the formation of olefins from alcohols by reaction with thionyl chloride proceeds *via* carbocations generated from the initially formed chlorosulphites. In some cases, the structures of such ions



SCHEME 3

can depend on that of the parent compounds. For instance, *cis*- and *trans*-4a-substituted decalins undergo elimination reactions through intermediate *cis*- and *trans*-like carbocations.[5,6] However in the present case the intermediacy of a common ionic species would not explain the formation of the same isomeric olefins in different ratios. Up to now, little attention has been paid to the role of ion pairs, but in our opinion the present results, in particular the unexpected formation of five isomeric olefins from (2), are better rationalized in terms of tight ion pairs, which arise from heterolysis of the chloro-sulphites (Scheme 4).

Compounds (3)—(5) can arise from the *cis*- (1) as well as the *trans*-isomer (2) *via* ion pairs [(13) and (14), respectively] and the corresponding carbocations. However only (13), owing to the presence in the 4a-position of an axial hydrogen atom in the *trans*-configuration relative to the counter ion, can rearrange into the ion pair (15), more stable for steric reasons, which in turn can afford the olefins (6) and (7) through the corresponding carbocation. In contrast, analogous rearrangement of (14) into (16) would be impossible because of the *cis*-configuration of the axial hydrogen atom at C-4a with respect to the counter ion.

Additional support for this mechanism was obtained from the results of reactions between the isomeric 4a-hydroxy-sulphones (10) and (11) with thionyl chloride.

TABLE 2

Distribution (%) of olefins in the reaction mixtures from the hydroxy-sulphones (10) and (11) with thionyl chloride

Hydroxy-sulphone	Temp.	Olefin	% Traces
(10)	Room temp.	(4)	27.0
	79 °C	(6)	46.0
		(7)	27.0
(11)	Room temp.	(4)	93.0
		(6)	3.5
		(7)	3.5
	79 °C	(4)	73.0
		(6)	20.0
		(7)	7.0

Both compounds furnished only (4), (6), and (7) in mixtures of different isomeric composition (Table 2 and Scheme 4). These results substantiate the hypothesis of the irreversible rearrangement of (13) into (15) and also that of the inhibited interconversion of (14) and (16).

Finally, it should be noted that thionyl chloride has no isomerizing effect on the olefins; hence the isomeric distributions reported in Tables 1 and 2 reflect kinetic control of the reactions.

[4] C. E. Boozer and E. S. Lewis, *J. Amer. Chem. Soc.*, 1953, **75**, 3182.

[5] A. F. Boschung, M. Geisel, and C. A. Grob, *Tetrahedron Letters*, 1968, 5169.

[6] G. E. Gream, *Austral. J. Chem.*, 1972, **25**, 1051.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded with a JEOL JNM 60 HL spectrometer (Me_4Si internal standard; solutions in $CDCl_3$), and i.r. spectra (Nujol mulls, unless otherwise noted) with a Perkin-Elmer 257 spectrophotometer. For analytical t.l.c., plates were coated with silica gel G (Merck) and developed with benzene–acetone (90 : 10). For chromatographic columns extra pure silica (Merck; 70—230 mesh ASTM) was used as stationary phase and benzene–acetone (90 : 10) as eluant.

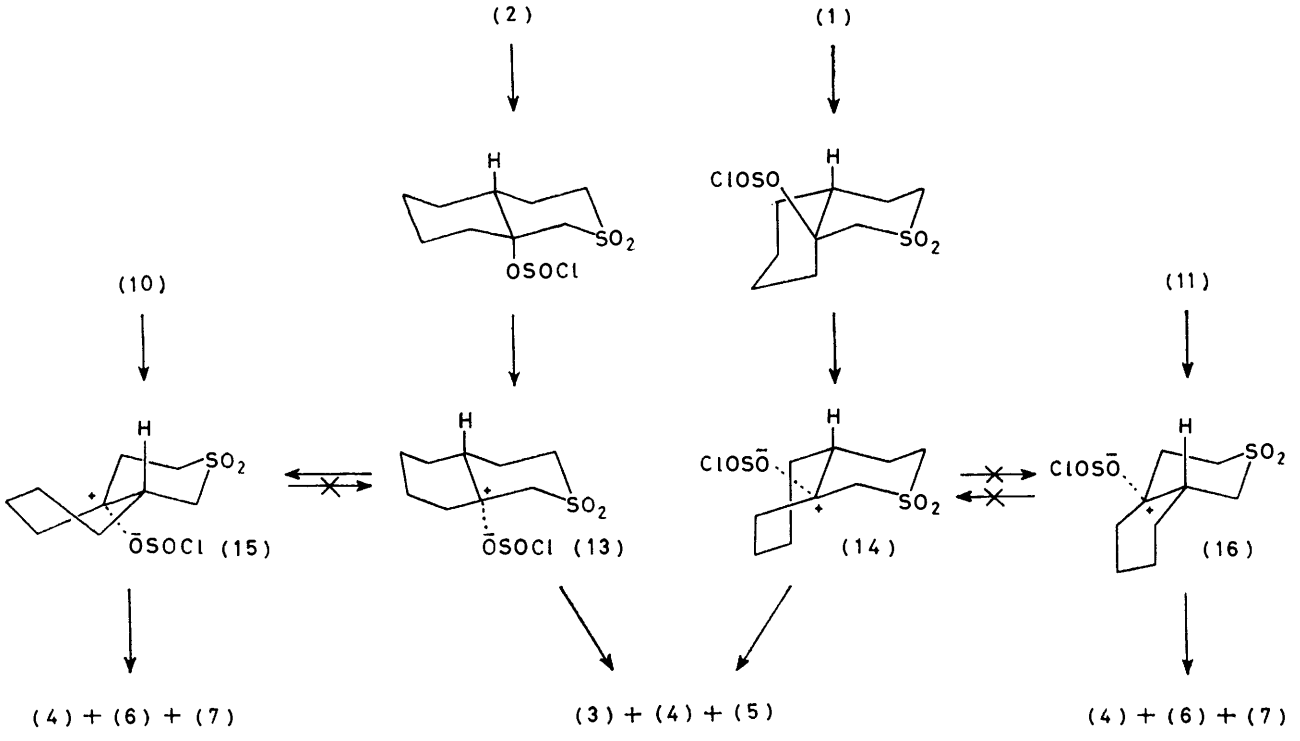
Reactions between Thionyl Chloride and the Hydroxy-sulphones (1), (2), (10), *and* (11). The sulphone (0.500 g) was dissolved in thionyl chloride (25 ml); the solution was maintained at room temperature for 48 h or was refluxed for 48 h. The thionyl chloride was removed under reduced pressure: the oily residue was dissolved in benzene and purified by passage through a short column of silica. After removal of the solvent the oily mixtures were submitted to elemental and spectroscopic analyses.

TABLE 3

Elemental analyses for the olefinic mixtures

Hydroxy-sulphone	Temp. (°C)	Found (%) C	Found (%) H	Required (%) for $C_9H_{14}O_2S$ C	Required (%) for $C_9H_{14}O_2S$ H
(1)	25	57.8	7.7		
(1)	79	57.9	7.6		
(2)	79	57.6	7.8	58.0	7.6
(10)	79	57.9	7.7		
(11)	25	57.8	7.6		
(11)	79	58.0	7.7		

Epoxidation of the Mixture from the Reaction of the cis-*Hydroxy-sulphone* (1) *with Thionyl Chloride*.—The oily mixture (0.400 g) was dissolved in diethyl ether, treated with monoperphthalic acid in ether, and maintained at room temperature for 48 h. T.l.c. revealed the presence of unchanged (3) and the known epoxides of (4) and (5).[1] The solvent was removed and the residue was treated with benzene; the phthalic acid was filtered off and the concentrated solution was subjected to repeated chromatography on silica.



SCHEME 4

The epoxide (8), m.p. 120 °C,[1] was isolated almost pure: the slower running fractions furnished a little of the epoxide of (5), m.p. 110 °C.[1]

cis- *and* trans-4a-*Hydroxy*-2-*thiadecalin* 2,2-*Dioxides* (10) *and* (11).—The hydroxy-sulphone (9) (2.1 g) was hydrogenated over platinum oxide in acetic acid for 12 h. After filtration, the solvent was removed *in vacuo* and the residue was chromatographed on silica. The first fractions furnished the *hydroxy-sulphone* (10) (0.600 g), m.p. 145—146 °C (from benzene–light petroleum) (Found: C, 53.0; H, 7.9. $C_9H_{16}O_3S$ requires C, 52.9; H, 7.9%); $\nu_{max.}$ ($CHCl_3$) 3 500 and 3 610 cm^{-1}; $\nu_{max.}$ (Nujol) 3 470 cm^{-1}; δ 2.1 (1 H, s, OH). Further elution furnished a mixture of (10) and (11) (0.2 g), and finally pure trans-*isomer* (11) (1.2 g), m.p. 92 °C (from benzene–light petroleum) (Found: C, 53.0; H, 8.0%); $\nu_{max.}$ ($CHCl_3$) 3 490 and 3 600 cm^{-1}; $\nu_{max.}$ (Nujol) 3 505 cm^{-1}; δ 2.45 (1 H, s, OH).

Acetyl Derivatives of the Hydroxy-sulphones (10) *and* (11).—(*a*) The *cis*-hydroxy-sulphone (10) (0.500 g) was refluxed with acetyl chloride (20 ml) for 8 h. The acetyl chloride was removed *in vacuo* and the solid *acetate* was recrystallised from ethanol; m.p. 134 °C (Found: C, 53.4; H, 7.5. $C_{11}H_{18}O_4S$ requires C, 53.6; H, 7.4%); $\nu_{max.}$ 1 725 cm^{-1} (CO).

(*b*) The *trans*-hydroxy-sulphone (11) (0.500 g) was left overnight at room temperature in acetyl chloride (20 ml). The solvent was removed and the solid *acetate* was crystallised from ethanol; m.p. 118 °C (Found: C, 53.3; H, 7.4%); $\nu_{max.}$ 1 725 cm^{-1} (CO).

Pyrolyses of the Acetyl Derivatives.—(*a*) The pyrolysis of the acetyl derivative of (10) (0.200 g) was performed at 450 °C in a combustion tube under a stream of nitrogen. An oily mixture was obtained (Found: C, 57.8; H, 7.6. Calc. for $C_9H_{14}O_2S$: C, 58.0; H, 7.6%); δ 5.80 (0.84 H, t, HC=C) (6) and 5.40 (0.16 H, m, HC=C) (7).

(*b*) The pyrolysis of the acetyl derivative of (11) was performed as in (*a*) to give an oily mixture (Found: C, 57.9; H, 7.7%); δ 5.80 (0.25 H, t, HC=C) (6) and 5.40 (0.25 H, m, HC=C) (7). Compound (4) [1] (50%) was identified by t.l.c. analysis and by epoxidation of the mixture.

2-*Thia*-$\Delta^{4a(5)}$-*octalin* 2,2-*Dioxide* (6).—The mixture obtained from pyrolysis of the acetyl derivative of (10) furnished by column chromatography the *olefin* (6), m.p. 75—76 °C (Found: C, 58.1; H, 7.6. $C_9H_{14}O_2S$ requires C, 58.0; H, 7.6%); $\nu_{max.}$ 1 665 cm^{-1} (C=C); δ 5.80 (1 H, t, HC=C).

The 4a,5-*Epoxide* (12).—The olefin (6) (0.150 g) dissolved in diethyl ether was treated with ethereal monoperphthalic acid and left at room temperature for 48 h. After evaporation and treatment with benzene to remove the phthalic acid, the solid *product* was recrystallised from ethanol; m.p. 134 °C (Found: C, 53.3; H, 6.9. $C_9H_{14}O_3S$ requires C, 53.5; H, 7.0%). The epoxide was unchanged after treatment with 10% aqueous potassium hydroxide for 2 h at room temperature. Overnight hydrogenation over platinum oxide in acetic acid furnished the *trans*-4a-hydroxysulphone (10).

Epoxidation of the Mixture from the Reaction of the Hydroxysulphone (2) *with Thionyl Chloride.*—The mixture (0.400 g) was dissolved in diethyl ether and treated with ethereal monoperphthalic acid. After 48 h at room temperature, t.l.c. revealed the presence of unchanged (3) and the epoxides of (4), (5), and (6). After the usual work-up, the mixture was repeatedly chromatographed; the epoxides, m.p. 120 °C [1] (8) [from (4)], m.p. 110 °C [1] [from (5)], and m.p. 134 °C (12) [from (6)] were isolated.

The last fractions containing the epoxide (8) revealed on g.l.c. analysis the presence of an unidentified product. I.r. and n.m.r. spectra and elemental analysis indicated that it was an epoxide. Attempts to separate this compound [presumably the epoxide of (7)] were unsuccessful.

Epoxidation of the Reaction Mixtures from the Hydroxysulphones (10) *and* (11) *with Thionyl Chloride.*—The mixtures were epoxidized under the conditions already described. The epoxides of (4) and (6) were detected and isolated. The epoxide of (7) was detected only by g.l.c. analysis.

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