STEREOCHEMISTRY OF FORMATION OF THIETANE, THIOLANE AND THIANE DERIVATIVES IN CYCLISATIONS OF DICHLORO ALCOHOLS AND CHLOROOXIRANES

J.ZÁBRANSKÝ[a,b], J.V.ČERNÝ[b], and P.SEDMERA[c]

[a] *Department of Organic Chemistry, Charles University, 128 43 Prague 2*
[b] *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 16 206 Prague 6 and*
[c] *Institute of Microbiology, Czechoslovak Academy of Sciences, 142 20 Prague 4*

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Cyclisation reactions of *threo*, *erythro*-3,5-dichloro-2-pentanol (*Ia*, *Ib*), *threo*, *erythro*-1,4-dichloro-3-pentanol (*Va*, *Vb*) and *cis*, *trans*-2-(2-chloroethyl)-3-methyloxirane (*IVa*, *IVb*) with potassium sulphide were studied. These cyclisations afforded *threo*, *erythro*-2-(1-hydroxyethyl)-thietane (*IIa*, *IIb*) and *cis*, *trans*-2-methyl-3-thiolanol (*VIIa*, *VIIb*). Cyclisations of *cis*, *trans*-2-(3-chloropropyl)-3-methyloxirane (*VIa*, *VIb*) gave *threo*, *erythro*-2-(1-hydroxyethyl)thiolane (*VIIIa*, *VIIIb*) and *cis*, *trans*-2-methyl-3-thianol (*IXa*, *IXb*). All the studied cyclisations are stereospecific: the oxiranes react with one and the alcohol *Ia*, *Ib* with two inversions of configuration. Five-membered ring is formed preferentially to four- or six-membered rings.

Cyclisation reactions of dichloro alcohols and oxirane derivatives with alkali metal sulphides have been reported to proceed unequivocally as far as the size of the formed ring is concerned: they afford either thietane[1-3] or thiolane[4-6] derivatives. Thus, the cyclisation of 3,5-dichloro-2-pentanol (*I*) was claimed[7] to give 2-(1-hydroxyethyl)thietane (*II*). On the other hand, according to Černý and Poláček[8] this reaction gives a non-homogeneous product.

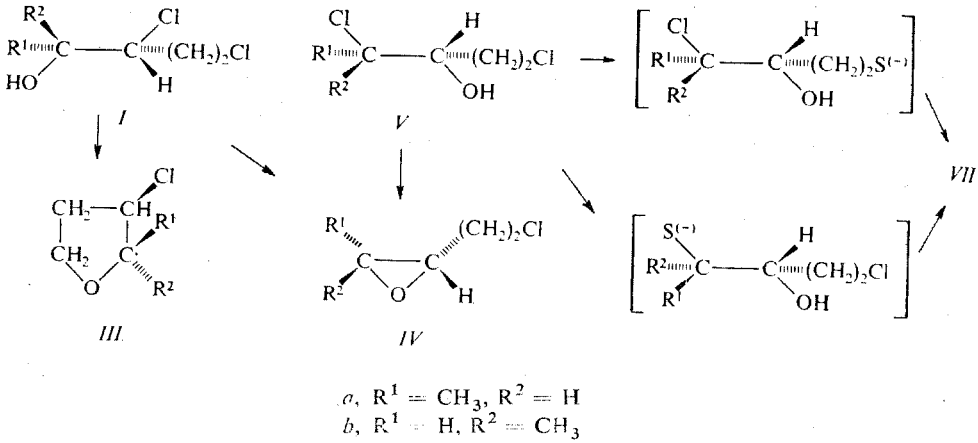
In order to study further these cyclisations we prepared a series of dichloro alcohols and chloro oxiranes. The alcohol *I*, prepared by reduction of 3,5-dichloro-2-pentanone with lithium aluminium hydride[8], represented a mixture of *threo*- and *erythro*-3,5-dichloro-2-pentanol (*Ia* and *Ib*) in the ratio 66 : 34. Its dehydrohalogenation by potassium hydroxide afforded *cis*- and *trans*-3-chloro-2-methyloxolane (*IIIa* and *IIIb*), and *cis*- and *trans*-2-(2-chloroethyl)-3-methyloxirane (*IVa* and *IVb*) in the ratio 11 : 7 : 58 : 24. A mixture of *threo*- and *erythro*-1,4-dichloro-3-pentanol (*Va* and *Vb*) in the ratio 62 : 38 was obtained by reduction of 1,4-dichloro-3-pentanone[9] with lithium aluminium hydride. A mixture (63 : 37) of *cis*- and *trans*-oxirane *IVa* and *IVb* was prepared by dehydrohalogenation of the alcohol *V* by potassium hydroxide.

The oxiranes *IVa* and *IVb*, as well as *cis*- and *trans*-2-(3-chloropropyl)-3-methyloxirane *VIa* and *VIb*, were also prepared from the corresponding unsaturated alcohols by reaction with thionyl chloride and epoxidation with monoperoxyphthalic acid. The stereoisomeric oxiranes *IVa*, *IVb* were prepared similarly from 3-penten-1-ol[10]. Since the separation of the oxiranes by preparative gas–liquid chromatography presented difficulties, the pure isomers were synthesized separately. The *cis*-oxirane *IVa* was prepared starting from *cis*-3-penten-1-ol which in turn was obtained from 3-pentyn-1-ol[11] by hydrogenation over P-2 nickel[12]. The *trans*-oxirane *IVb* was synthesized from *trans*-3-penten-1-ol[13] which was prepared by reduction of 3-pentyn-1-ol with sodium in liquid ammonia. The *cis*-oxirane *VIa* was prepared from *cis*-4-hexen-1-ol which was obtained by hydrogenation of 4-hexyn-1-ol[14] over nickel P-2. *trans*-4-Hexen-1-ol, required for the preparation of the trans-oxirane *VIb*, was prepared by reaction of 3-chloro-2-methyloxane[14] with sodium powder.

The reaction of *cis*-oxirane *IVa* with potassium sulphide afforded *threo*-2-(1-hydroxyethyl)thietane (*IIa*) and *cis*-2-methyl-3-thiolanol (*VIIa*) in the ratio 21 : 79. Reaction of the *trans*-oxirane *IVb* led to a mixture of *erythro*-2-(1-hydroxyethyl)-thietane (*IIb*) and *trans*-2-methyl-3-thiolanol (*VIIb*) in the ratio 14 : 86. The mixture of the *threo*- and *erythro*-alcohols *Ia* and *Ib* afforded with potassium sulphide a product exhibiting the same physical constants and IR spectrum as described in the literature[7,8]. We found that this product contains four compounds, thietanes *IIa*, *IIb* and thiolanes *VIIa*, *VIIb*, in the ratio 21 : 9 : 45 : 25. Cyclisation of the mixture of *threo* and *erythro* alcohols *Va*, *Vb* afforded also a mixture of compounds *IIa*, *IIb*, *VIIa* and *VIIb*, in the ratio 16 : 12 : 40 : 32. The *cis*-oxirane *VIa* was transformed by the reaction with potassium sulphide into the mixture of *threo*-2-(1-hydroxyethyl)-thiolane (*VIIIa*) and *cis*-2-methyl-3-thianol (*IXa*) in the ratio 60 : 40. Finally, cyclisation of the *trans*-oxirane *VIb* gave *erythro*-2-(1-hydroxyethyl)thiolane (*VIIIb*) and *trans*-2-methyl-3-thianol (*IXb*) in the ratio 61 : 39.

The configuration of the alcohols *Ia*, *Ib* and *Va*, *Vb* was assigned on the basis of the known stereochemistry of the dehydrohalogenation reaction (Scheme 1). The configuration of the stereoisomeric oxiranes *IVa*, *IVb* and *VIa*, *VIb* was elucidated by ^{1}H-NMR spectroscopy using the different chemical shifts of the oxirane[15] and methyl[16] protons. Due to a steric repulsion[17] the *cis*-oxirane *IVa* exhibits a greater coupling constant J_{CH_3-CH} than the *trans*-oxirane *IVb*. The thietanes *II* and thiolanes *VII*, and analogously thiolanes *VIII* and thianes *IX*, were distinguished on the basis of the different chemical shifts of the methine protons in the groupings $CH_3—\underset{|}{C}H—O$ and $CH_3—\underset{|}{C}H—S$. *cis*- and *trans*-Thiolanes *VIIa*, *VIIb* and *cis* and *trans*-thianes *IXa*, *IXb* were distinguished using differences in the vicinal coupling constants of methine protons in five- and six-membered rings[18] and differences in the chemical shifts of methyl protons in five-membered rings caused by the vicinal hydroxyl[19]. From the

width of the multiplet due to the methine proton CH—OH it follows that this proton is equatorial in the *cis*-thiane *IXa* and axial in the *trans*-thiane[18] *IXb*.



SCHEME 1

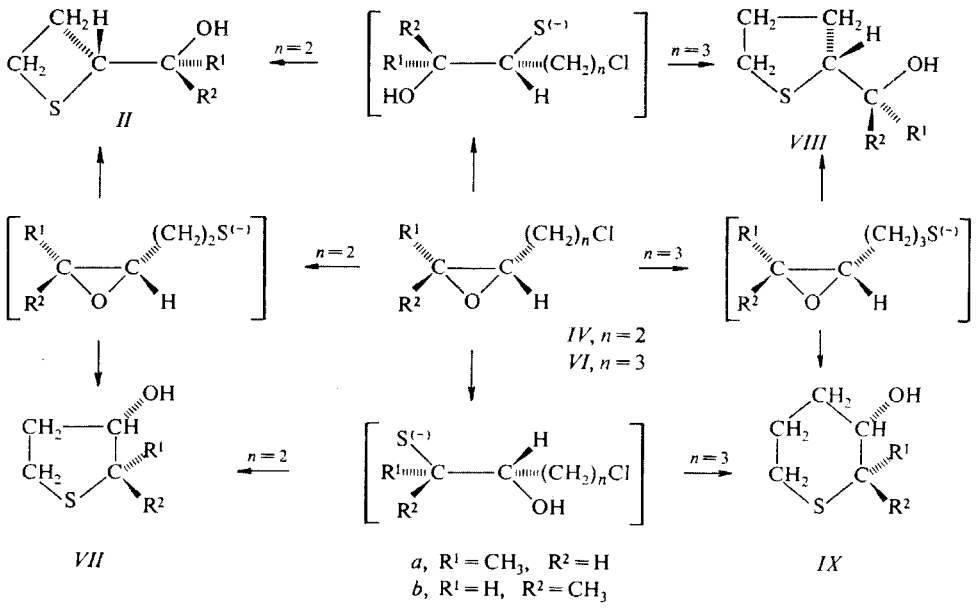
The conclusions concerning ring size were proved by mass spectrometry. The spectra of the thietanes *II* and thiolanes *VIII* exhibit ions $(M—CH_3CHO)^+$ and $(M—CH_3CHOH)^+$. Further, the spectra of thietanes *II* display peaks due to the ions $CH_2S^{(+)}$ and $CHS^{(+)}$ which arise in the fission of the thietane ring[20]. Thiolanes *VII* give rise to the ion $C_3H_6S^{(+)}$, which is formed by the fission of the $C_{(2)}—C_{(3)}$ and $C_{(4)}—C_{(5)}$ bonds, and ions $C_2H_5S^{(+)}$ and $C_3H_5O^{(+)}$ from the fission of $C_{(2)}—C_{(3)}$ and $C_{(5)}—C_{(1)}$ bonds (fragmentation according to ref.[21,22]). The spectrum of the thiane *IX* contains signal due to $(M—C_2H_5)^+$, ions $C_3H_7S^{(+)}$ and $C_3H_5O^{(+)}$, arising in the fission of $C_{(2)}—C_{(3)}$ and $C_{(5)}—C_{(6)}$ bonds, and an ion $C_2H_5S^{(+)}$. This is in accord with the fact that the mass spectrum of thiane exhibits an ion $(M—C_2H_5)^+$ which is not present in the spectrum of thiolane[21] and that 2-hydroxymethylthiolane does not give rise to the $C_2H_5S^{(+)}$ ion, whereas in the spectrum of 3-thianol the signal due to this ion is abundant[22]. Detection of the intramolecular hydrogen bond OH···S was used[23] in the assignment of configuration to the *threo*- and *erythro*-isomers of thietane (*IIa*, *IIb*) and thiolane (*VIIIa*, *VIIIb*), similarly as in the case of analogous oxolane derivatives[24]. Thanks to the anticlinal conformation of methyl and methylene in the position 3 in the *threo*-isomers, the conditions for hydrogen bond formation in them are more favourable than in the *erythro*-isomers where the methyl group is in a synperiplanar conformation. The presence of methyl in a position similar to an equatorial position in cyclohexane makes the hydrogen bond in the *cis*-thiolane *VIIa* more advantageous as compared with that in the *trans*-thiolane *VIIb* in which the methyl occupies a conformation similar to an axial position in cyclohexane. In the *cis*-thiane *IXa* with a relatively greater population of the hydrogen bonded

hydroxyl the preponderant conformation is OH-axial, CH_3-equatorial; however, also a twisted boat conformation cannot be excluded. Since the C—S bond is longer than the C—C bond, the twist-boat conformation of the ring becomes more flexible, its torsion angles near to 60° and the methyl group is in an antiperiplanar conformation. As seen on Dreiding models, in this conformation there is a shorter H···S distance (2·2 Å) than in the chair form (2·4 Å). *trans*-Thiane *IXb* exists predominantly in the diequatorial conformation, the amount of the diaxial form being only small.

We explain the formation of the thiolane *VII* in the cyclisation of the alcohol *I* and the formation of the thietane *II* from the alcohol *V* by the reaction *via* the oxirane *IV*. The cyclisation proceeds with two inversions of configuration at the diastereoisomeric center of the alcohol *I* or *V* during the closure and opening of the oxirane ring. Accordingly, the ratio of the starting isomers in *I* is the same as the ratio of the products (*IIa* + *VIIa* : *IIb* + *VIIb* = 66 : 34). Cyclisations of 1,4-dichloroalkanes[25,26] are more facile than those of 1,3-dichloroalkanes[27]. The former reaction takes place concurrently in the cyclisation of the alcohol *V*. The stereochemistry of this reaction without participation of the hydroxyl group is opposite to that of the reaction via the oxirane ring, since in this case there is only one inversion of configuration – the substitution of the secondary chlorine with hydrosulphide or thiolate ion (Scheme 1). As a result of competition of both reactions the ratio of the products (*IIa* + *VIIa* : : *IIb* + *VIIb* = 56 : 44) is lower than the ratio of the starting stereoisomeric alcohols *V*. The unequivocality of the cyclisations of 1,4-dichloro-2-butanol[4] and 1,4-dichloro-2,3-butanediol[5] is caused by the fact that the intermediate oxirane has no alkyl in the position 3 and therefore the nucleophilic reagent enters exclusively into this position.

We have suggested two reaction paths for the cyclisations of the studied oxiranes *IV* and *VI* (Scheme 2). The first alternative is a primary attack of the oxirane ring with the hydrosulphide ion, followed by an intramolecular cyclisation. The second alternative represents a primary substitution of chlorine with the sulphide ion, followed by an intramolecular cyclisation. In the first scheme the ratio of the arising rings is determined by the first step, in the second reaction path by the second step. The stereochemistry of both the reaction paths is identical, since only one inversion of configuration at the diastereoisomeric center takes place. The first mechanism is supported by the isolation of 3-chloro-2-hydroxy-1-propanethiol in the reaction of 2-chloromethyloxirane with sodium hydrosulphide[2]. The fact that in intramolecular cyclisations of *trans*-oxiranes the formation of five-membered rings is preferred to the formation of the four-membered[28] and six-membered[16] rings supports the second mechanism. On the other hand, the *cis*-isomers of the mentioned oxiranes afford only smaller of the two rings. This effect was to a small extent observed in the cyclisation of the oxiranes *IV* but not in the reaction of oxiranes *VI*. The unequivocal cyclisation of *trans*-3,4-epoxycyclopentenylmethyl-4-bromobenzenesulphonate[6] is given by the symmetry of the molecule, since in this case the substitution at the posi-

tions 3 and 4 by the nucleophilic reagent leads only to enantiomers of the product. The whole problem is described and discussed in detail elsewhere[29].



SCHEME 2

EXPERIMENTAL

The IR spectra were taken on a Perkin-Elmer 457 spectrophotometer (film), the spectra of very dilute solutions were taken in 40 mm cells on a Pye-Unicam SP 700 instrument. The ^{1}H-NMR measurements were performed on a Tesla BS-487 (80 MHz) spectrometer with hexamethyldisiloxane, compounds *I*, *VIIIa*, *IXa* on a Varian HA-100 instrument with tetramethylsilane. The mass spectra were measured on a MCH-1303 spectrometer, 100 eV, using direct inlet. Gas–liquid analyses were performed on a Chrom 31 (Laboratorní přístroje, Prague) chromatograph with flame-ionisation detector, nitrogen flow 45—75 cm^3/min, stainless steel columns packed either with 10% GE-XE-60 on Chromaton N-AW-DMCS 0·25—0·30 mm, length 2·4 m, diameter 6 mm, or with 4% poly(ethylene glycol adipate) (PEGA) on firebrick 0·2—0·3 mm, length 1·2 m, diameter 6 mm. Preparative gas–liquid chromatography was carried out using a 5 m stainless steel column packed with 10% GE-XE-60 on Chromaton N-AW-DMCS 0·25—0·30 mm, diameter 6 mm, nitrogen flow rate 75—100 cm^3/min. Gas–liquid chromatographic analyses of the mixtures of the alcohols *VIIIa* and *IXa* were performed on a Perkin-Elmer F-30 chromatograph with flame-ionisation detector, nitrogen flow rate 30 cm^3/min, on a stainless column with 5% sodium 3-aminobenzenesulphonate and 15% poly(ethylene glycol) 600 on Cellite 60/80 (3-aminobenzenesulphonate was adsorbed first on the carrier in methanolic solution). The preparative separation of the mixtures of *VIIIa* and *IXa* was accomplished on a Perkin-Elmer 900 instrument using the same packing as used in the analytical experiments (nitrogen flow rate 50 cm^3/min, column length 1·8 m, diameter 4·4 mm).

3,5-Dichloro-2-pentanol (*I*)

This compound was prepared according to ref.[8] in 80% yield; b.p. 92·5–93°C/13 Torr, n_D^{20} 1·4770 (ref.[8] states b.p. 84–90°C/12 Torr, n_D^{20} 1·4726). The product contained 99% of *I* (1% of oxolane *III*) and consisted of 66% *threo* and 34% *erythro* isomer, according to gas–liquid chromatography (GE-XE-60, 120°C, R_t 18·2 and 21·2 min; PEGA, 120°C, R_t 20·7 and 24·8 min). Separation of the isomers by preparative gas–liquid chromatography was not possible. IR spectrum (film, cm^{-1}): 650 (C—Cl primary), 688 (C—Cl secondary), 735 (C—Cl primary), 785 (C—Cl secondary), 3390 (OH). ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·82–4·34 (m, 2 H, CH—Cl and CH—O), 3·76 (t, J = 7 Hz, 2 H, CH_2—Cl), 2·11–2·47 (m, 2 H, C—CH_2—C), 1·91 (s, 1 H, OH), 1·32 (d, J = 6 Hz, 3 H, CH_3 *threo*), 1·28 (d, J = 6·2 Hz, 3 H, CH_3 *erythro*). Mass spectrum, *m/e* (relative intensity, %): 156 (–) M^+, 45 (100) $(C_2H_5O)^+$, 42 (21).

Dehydrohalogenation of 3,5-Dichloro-2-pentanol (*I*) by Potassium Hydroxide

3,5-Dichloro-2-pentanol (*I*) (46·5 mg, 0·295 mmol; 34% *erythro*, 66% *threo*) was mixed at room temperature with a potassium hydroxide solution (0·29 ml, 0·75 mmol) prepared by dissolving potassium hydroxide (8·70 g, 0·155 mol) in water (28 ml) and ethanol (25 ml). The mixture was shaken for 30 min at the same temperature and the separated potassium chloride centrifuged. The mixture was extracted with ether (5 × 0·1 ml), dried over anhydrous magnesium sulphate and concentrated under diminished pressure. According to gas–liquid chromatographic analysis (GE-XE-60, 80°C; PEGA, 100°C) the product contained *trans*- and *cis*-3-chloro-2-methyloxolane (*IIIb*, *IIIa*) and *trans*- and *cis*-2-chloroethyl-3-methyloxirane (*IVb*, *IVa*) in the ratio 7 : 11 : 24 : 58 (comparison with authentic standards).

1,4-Dichloro-3-pentanol (*V*)

This compounds was prepared from 1,4-dichloro-3-pentanone in 82% yield similarly as described for *I*; b.p. 87–88°C/15 Torr, n_D^{20} 1·4780. The product contained 10% lower-boiling impurities, the ratio of *threo*- and *erythro* isomers was 62 : 38 as found by gas–liquid chromatography (GE-XE-60, 120°C, R_t 18·1 and 21·6 min). The product was purified by preparative gas–liquid chromatography (GE-XE-60, 145°C, 16–26 min). IR spectrum (film, cm^{-1}): 650 (C—Cl primary), 688 (C– Cl secondary), 735 (C—Cl primary), 786 (C—Cl secondary), 3390 (OH). ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·87 (bs, 1 H, OH), 3·80–4·28 (m, 2 H, CH—Cl and CH—O), 3·71 (t, J = 7 Hz, 2 H, CH_2Cl), 1·72–2·20 (m, 2 H, C—CH_2—C), 1·56 (d, J = 6 Hz, 3 H, CH_3 *erythro*), 1·48 (d, J = 5·8 Hz, 3 H, CH_3 *threo*). Mass spectrum, *m/e* (relative intensity %): 156 (–) M^+, 95 (31), 93 (100) $(M - C_2H_4Cl)^+$, 57 (18) $(M - HCl)^+$. For $C_5H_{10}Cl_2O$ (157·0) calculated: 38·24% C, 6·42% H, 45·15% Cl; found: 38·52% C, 6·55% H, 44·89% Cl.

5-Chloro-2-pentene

Prepared according to ref.[30] in 44% yield, b.p. 107–109°C, n_D^{20} 1·4378 (ref.[30] reports b.p. 107–107·5°C, n_D^{20} 1·4310). GLC analysis showed 65% *trans*- and 35% *cis*-isomer (GE-XE-60, 60°C, R_t 3·0 and 3·5 min.). IR spectrum (film, cm^{-1}): 654 (C—Cl), 729 (C—Cl), 965 (C=CH *trans*). ^{1}H-NMR spectrum (tetrachloromethane, δ): 5·45 (m, 2 H, $C_{(2)}$ and $C_{(3)}$), 3·43 (t, J = = 7 Hz, 2 H, CH_2Cl), 2·45 (m, 2 H, $C_{(4)}$), 1·68 (m, 3 H, CH_3). For C_5H_9Cl (104·6) calculated: 57·43% C, 8·67% H, 33·90% Cl; found: 57·17% C, 8·82% H, 33·74% Cl.

2-(2-Chloroethyl)-3-methyloxirane (*IV*)

a) *From 5-chloro-2-pentene*: A mixture of an 0·802M ethereal solution of monoperoxyphthalic acid (715 ml) and 5-chloro-2-pentene (30 g; 0·287 mol; 35% cis, 65% trans) was set aside for 10 days at about 3°C. The separated phthalic acid was filtered off, the filtrate neutralised with 20% sodium carbonate solution (450 ml), washed with water (150 ml) and dried over anhydrous magnesium sulphate. The ether was evaporated under diminished pressure and the residue distilled, affording 24·4 g (70%) of *IV*, b.p. 44—48°C/13 Torr, n_D^{20} 1·4394. According to gas–liquid chromatography the product contained 68% *trans*- and 32% *cis*-isomer (GE-XE-60, 80°C, R_t 14·3 and 18·6 min; PEGA, 100°C, R_t 7·8 and 10·4 min), purity 99%. Separation of the isomers by preparative gas–liquid chromatography (GE-XE-60, 90°C, 49—56, 65—71 min) afforded:

trans-2-(2-*Chloroethyl*)-3-*methyloxirane* (IVb): IR spectrum (film, cm^{-1}): 420 w, 465 w, 482 w, 512 s, 656 s (C—Cl), 715 s (C—Cl), 750 w, 772 w, 805 m, 830 m, 868 s, 918 m, 941 s, 960 m, 993 m, 1122 s, 1066 w, 1076 w, 1092 m, 1128 m, 1148 m, 1238 m, 1255 m, 1290 s, 1353 m, 1380 s, 1418 m, 1455 s, 1478 m, 1623 m, 2870 m, 2926 s, 2964 s, 2984 s. ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·65 (t, J = 6·5 Hz, 2 H, CH_2—Cl), 2·81 (m, 2 H, $C_{(2)}$ and $C_{(3)}$), 1·96 (m, 2 H, C—CH_2—C), 1·32 (d, J = 4·5 Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 120 (2·5) M^+, 104 (3) $(M - O)^+$, 93 (4) $(M - C_2H_3)^+$, 91 (4) $(M - C_2H_5)^+$, 85 (81) $(M - Cl)^+$, 71 (100) $(M - CH_2Cl)^+$, 57 (56) $(C_3H_5O)^+$, 55 (72), 45 (65), 44 (27), 43 (59), 41 (45). Intensity of the isotopic ion M + 2 calculated: 33·0%; found: 29·2%. For C_5H_9ClO (120·6) calculated: 49·81% C, 7·52% H, 29·40% Cl; found: 49·49% C, 7·50% H, 29·28% Cl.

cis-2-(2-*Chloroethyl*)-3-*methyloxirane* (IVa): IR spectrum (film, cm^{-1}): 405 w, 460 m, 476 s, 726 m, 745 m, 655 s (C—Cl), 713 s (C—Cl), 725 m, 772 s, 799 m, 830 m, 864 s, 890 m, 921 s, 966 m, 991 m, 1022 m, 1066 s, 1113 w, 1140 m, 1150 m, 1178 w, 1213 w, 1241 m, 1272 m, 1293 s, 1323 m, 1368 s, 1392 s, 1450 s, 1715 m, 2890 m, 2930 s, 2970 s, 2990 s. ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·70 (t, J = 7·5 Hz, 2 H, CH_2—Cl), 3·11 (m, 2 H, $C_{(2)}$ and $C_{(3)}$), 1·99 (m, 2 H, C—CH_2—C), 1·29 (d, J = 5 Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 120 (3·2), 104 (5), 93 (4), 91 (4), 85 (72), 71 (100), 57 (59), 55 (60), 45 (65), 44 (36), 43 (60), 41 (45). For the assignment of the ions see the *trans*-isomer. The intensity of the isotopic ion M + 2 calculated: 33·0%; found: 31·9%. For C_5H_9ClO (120·6) calculated: 49·81% C, 7·52% H, 29·40% Cl; found: 49·55% C, 7·59% H, 29·30% Cl.

b) *From* 1,4-*dichloro*-3-*pentanol* (V): A mixture of 1,4-dichloro-3-pentanol (*V*) (3·90 g, 24·8 mmol; 38% *erythro*, 62% *threo*), was mixed at room temperature with a potassium hydroxide solution prepared by dissolving potassium hydroxide (2·50 g, 44·5 mmol) in water (8 ml) and ethanol (5 ml). The mixture was stirred at the same temperature, extracted with ether (3 × 4 ml) and the extract dried over anhydrous magnesium sulphate. The ether was evaporated under diminished pressure and the residue distilled, affording 2·78 g (71%) of the oxirane *IV*. b.p. 44—47°C/13 Torr. According to gas–liquid chromatography the product was 99% pure and contained 37% *trans*- and 63% *cis*-isomer. The retention times of both the isomers were identical with the isomeric oxiranes *IV*, prepared according to *a*). The *cis*- and *trans*-isomers were separated by preparative gas–liquid chromatography and were identical with the compounds prepared according to *a*).

cis-3-Penten-1-ol

A solution of sodium borohydride (0·558 g, 14·8 mmol) in 95% ethanol (15 ml), followed by ethylenediamine (1·65 ml) and 3-pentyn-1-ol (8·41 g, 100 mmol) was added successively under hydrogen to a stirred solution of nickel acetate tetrahydrate (3·12 g; 12·6 mmol) in 95% ethanol (120 ml).

After consumption of the corresponding amount of hydrogen the hydrogenation almost stopped (90 min). The catalyst was removed by mixing with charcoal and subsequent centrifuging or filtration, water (300 ml) was added to the filtrate and the product was taken up into ether (5 × 30 ml). The extract was washed with water (30 ml), dried over anhydrous magnesium sulphate and the solvents were evaporated under diminished pressure, yielding 6·97 g (81%) of *cis*-3-penten-1-ol, n_D^{20} 1·4374 (ref.[13] reports n_D^{20} 1·4386), which contained less than 1% of *trans*-isomer (gas–liquid chromatography on GE-XE-60, 80°C). IR spectrum (film) was identical with the spectrum published in ref.[31]. For $C_5H_{10}O$ (86·1) calculated: 69·72% C, 11·70% H; found: 69·98% C, 11·61% H.

cis-5-Chloro-2-pentene

This compound was prepared in 40% yield from *cis*-3-penten-1-ol similarly as described for the mixture of *cis*- and *trans*-isomers; b.p. 105—110°C, n_D^{20} 1·4394. The product contained less than 1% *trans*-isomer (gas–liquid chromatography on GE-XE-60, 60°C). IR spectrum (film, cm^{-1}): 576 (C=C *cis*), 660 (C—Cl), 680, 700 (C=CH *cis*), 736 (C—Cl), 1655 (C=C *cis*). For C_5H_9Cl (104·6) calculated: 57·43% C, 8·67% H, 33·90% Cl; found: 57·41% C, 8·75% H, 33·81% Cl.

cis-2-(2-Chloroethyl)-3-methyloxirane (*IVa*)

The compound was prepared in 61% yield from *cis*-5-chloro-2-pentene analogously to the preparation of the mixture of *cis*- and *trans*-isomer *IVa IVb*; b.p. 46—48°C/13 Torr. Purity 99%, contained less than 1% *trans*-isomer (gas–liquid chromatography, GE-XE-60, 80°C; PEGA, 100°C). The retention time of the product was identical with that of *IVa* obtained by the separation of isomers. The product was purified by preparative gas–liquid chromatography (GE-XE-60, 100°C, 41—47 min). IR spectrum was identical with the compound prepared according to *a*).

trans-5-Chloro-2-pentene

Prepared in 32% yield from *trans*-3-penten-1-ol as described for the mixture of isomers; b.p. 104—108°C, n_D^{20} 1·4358 (ref.[32] reports b.p. 108—109°C, 1·4360). Gas–liquid chromatography (GE-XE-60, 60°C) showed that the product was free of *cis*-isomer. IR spectrum (film, cm^{-1}): 654 (C—Cl), 728 (C—Cl), 965 (C=CH *trans*). C_5H_9Cl (104·6) calculated: 57·43% C, 8·67% H, 33·90% Cl; found: 57·60% C, 8·73% H, 34·07% Cl.

trans-2-(2-Chloroethyl)-3-methyloxirane (*IVb*)

Prepared from *trans*-5-chloro-2-pentene in 63% yield similarly as described for the mixture of isomers, b.p. 44—46°C/13 Torr. Purity 99% contains less than 1% *trans*-isomer (gas–liquid chromatography, GE-XE-60, 80°C; PEGA, 100°C). The product was purified by preparative gas–liquid chromatography (GE-XE-60, 100°C, 31—36 min) and its IR spectrum was identical with the spectrum of oxirane *IVb* prepared under *a*).

cis-4-Hexen-1-ol

Prepared in 86% yield from 4-hexyn-1-ol analogously as described for *cis*-3-penten-1-ol; n_D^{20} 1·4470 (ref.[14] 1·4420). Contains 1% *trans*-isomer (gas–liquid chromatography, GE-XE-60, 85°C, R_t 7·1 min). IR spectrum was identical with the spectrum described in ref.[14]. For $C_6H_{12}O$ (100·2) calculated: 71·95% C, 12·08% H; found: 72·32% C, 12·17% H.

cis-6-Chloro-2-hexene

Prepared in 47% yield from *cis*-4-hexen-1-ol similarly as described for 5-chloro-2-pentene, b.p. 130–132°C, n_D^{20} 1·4480. Contained 1% *trans*-isomer (gas–liquid chromatography on GE-XE-60, 60°C, R_t 7·1 min). IR spectrum (film, cm^{-1}): 578 (C=C *cis*), 650 (C—Cl), 700 (C=CH *cis*), 736 (C—Cl), 1655 (C=C *cis*). For $C_6H_{11}Cl$ (118·6) calculated: 60·76% C, 9·35% H, 29·89% Cl; found: 60·91% C, 9·26% H, 30·11% Cl.

cis-2-(3-Chloropropyl)-3-methyloxirane (*VIa*)

Prepared in 71% yield from *cis*-6-chloro-2-hexene analogously as described for the oxirane *IV*, b.p. 65–68°C/12 Torr. Purity 97%, contained 2% *trans*-isomer (gas–liquid chromatography on GE-XE-60, 95°C, R_t 16·4 min). The product was purified by preparative gas–liquid chromatography (GE-XE-60, 115°C, 37–42 min). IR spectrum (film, cm^{-1}): 418 w, 463 m, 480 m, 525 w, 540 w, 650 s (C—Cl), 718 s (C—Cl), 740 w, 759 m, 770 m, 784 m, 813 s, 824 s, 845 m, 858 w, 870 w, 906 s, 930 m, 960 m, 979 s, 1013 m, 1072 s, 1137 s, 1150 s, 1179 m, 1206 m, 1226 w, 1272 s, 1310 s, 1325 w, 1355 m, 1370 m, 1391 s, 1434 m, 1444 s, 1625 m, 1725 m, 2870 s, 2930 s, 2970 s, 3000 s. ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·61 (*t*, J = 6·5 Hz, 2 H, CH_2Cl), 3·11 (dq, $J_{2,3}$ = 0·8 Hz, 1 H, $C_{(3)}$), 2·87 (m, 1 H, $C_{(2)}$), 1·47–2·02 (m, 4 H, C—CH_2—C), 1·28 (d, J = 5·2 Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 134 (0·9) M^+, 119 (2) $(M - CH_3)^+$, 118 (2) $(M - O)^+$, 106 (1), 105 (2), 100 (6), 99 (77) $(M - Cl)^+$, 91 (23) $(C_4H_8Cl)^+$, 85 (48) $(M - CH_2Cl)^+$, 72 (30) $(M - C_2H_3Cl)^+$, 71 (89) $(M - C_2H_4Cl)^+$, 62 (22) $(C_2H_4Cl)^+$, 57 (37) $(C_3H_5O)^+$, 55 (66), 45 (56), 43 (100), 41 (74). Intensity of the isotopic ion M + 2 calculated: 33·0%, found: 41·5%. For $C_6H_{11}ClO$ (134·6) calculated: 53·54% C, 8·24% H, 26·34% Cl; found: 53·25% C, 8·18% H, 26·17% Cl.

trans-6-Chloro-2-hexene

Prepared in 55% yield from *trans*-4-hexen-1-ol similarly as described for 5-chloro-2-pentene; b.p. 129–131°C, n_D^{20} 1·4408 (ref.[32] reports b.p. 134–135°C, n_D^{20} 1·4418). According to gas–liquid chromatography (GE-XE-60, 60°C, R_t 6·4 min) the product was free of *cis*-isomer. IR spectrum (film, cm^{-1}): 652 (C—Cl), 725 (C—Cl), 967 (C=CH *trans*). For $C_6H_{11}Cl$ (118·6) calculated: 60·76% C, 9·35% H, 29·89% Cl; found: 60·48% C, 9·19% H, 30·17% Cl.

trans-2-(3-Chloropropyl)-3-methyloxirane (*VIb*)

Prepared in 78% yield from *trans*-6-chloro-2-hexene analogously as described for the oxirane *IV* b.p. 64–65°C/13 Torr. Purity 98%, contained 2% *cis*-isomer (gas–liquid chromatography on GE-XE-60, 95°C, R_t 13·8 min). The product was purified by preparative gas–liquid chromatography (GE-XE-60, 115°C, 28–33 min). IR spectrum (film, cm^{-1}): 401 w, 471 m, 482 w, 518 m, 650 s (C—Cl), 715 (C—Cl), 760 m, 775 m, 805 m, 858 s, 834 w, 908 s, 932 m, 964 m, 1024 s, 1049 m, 1080 m, 1096 s, 1128 m, 1146 m, 1206 w, 1226 w, 1252 m, 1238 s, 1291 s, 1339 s, 1380 s, 1444 s, 1480 m, 1616 w, 1720 m, 2868 s, 2930 s, 2960 s, 2980 s. ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·59 (t, J = 6 Hz, 2 H, CH_2—Cl), 2·56–2·94 (m, $J_{2,3}$ = 2 Hz, 2 H, $C_{(2)}$ and $C_{(3)}$), 1·47–2·09 (m, 4 H, C—CH_2—CH_2—C), 1·30 (d, J = 5·8 Hz, $^4J_{CH_3,C_{(2)}}$ = = 0·2 Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 134 (0·5), 119 (1), 118 (1), 106 (1), 105 (1), 100 (6), 99 (78), 91 (2), 85 (45), 72 (32), 71 (75), 62 (26), 57 (30), 55 (54). 45 (63), 43 (100), 41 (63). For the assignment of ions see the *cis*-isomer. Intensity of the isotopic ion peak M + 2 calculated: 33·0%; found: 29·8%. For $C_6H_{11}ClO$ (134·6) calculated: 53·54% C, 8·24% H, 26·34% Cl; found: 53·41% C, 8·30% H, 26·14% Cl.

Cyclisation of *cis*-2-(2-Chloroethyl)-3-methyloxirane (*IVa*) by Potassium Sulphide

A solution of potassium hydroxide (6·73 g, 0·12 mol) in water (16 ml) was saturated with hydrogen sulphide at 0°C, mixed with a solution of potassium hydroxide (6·73 g) in water (40 ml) at the same temperature and the obtained solution of potassium sulphide was diluted with ethanol up to 120 ml. To this solution (28 ml, 28 mmol) *cis*-2-(2-chloroethyl)-3-methyloxirane (*IVa*) (2·50 g, 20·8 mmol) was added dropwise during 10 min at room temperature under stirring, the temperature was rised in the course of one hour to 60°C and the mixture was stirred at this temperature for 30 minutes. The ethanol was evaporated under diminished pressure, water (25 ml) was added and the product was extracted with ether (5 × 8 ml). The ethereal solution was dried over anhydrous magnesium sulphate, the ether evaporated under diminished pressure and the residue distilled, affording 1·57 g (64%) of a liquid, b.p. 83–86°C/13 Torr. Gas–liquid chromatography showed 26% *IIa*, 72% *VIIa*, 2% *VIIb*. Further experiments resulted in the following isomer ratios 17 : 82 : 1 and 32 : 67 : 1 (GE-XE-60, 105°C, R_t 8·3, 14·2, 17·2 min). The mixture was separated by preparative gas–liquid chromatography (GE-XE-60, 130°C, 17–21, 28–37 min) affording: threo-2-(1-*Hydroxyethyl*)*thietane* (IIa): IR spectrum (film, cm^{-1}): 419 w, 475 m, 566 m, 685 m, 805 m, 858 s, 910 s, 952 s, 965 m, 1011 s, 1050 s, 1104 s, 1142 s, 1175 m, 1205 m, 1215 m, 1260 s, 1370 s, 1437 m, 1452 m, 1634 m, 2860 s, 2930 s, 2960 s, 3390 s. IR spectrum (tetrachloromethane, $5 . 10^{-3}$M, cm^{-1}): 3524 (OH bonded), 3624 (OH free), integrated intensity ratio 4·9 : 1. ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·77 (m, $J_{2,CH-O} = 4·8$ Hz, 1 H, CH—O), 3·65 (m, 1 H, $C_{(2)}$), 2·65–3·21 (m, 4 H, $C_{(3)}$ and $C_{(4)}$), 2·27 (bs, 1 H, OH), 1·05 (d, $J = 6·5$ Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity %): 118 (63) M^+, 75 (10), 74 (100) $(C_3H_6S)^+$, 73 (64) $(C_3H_5S)^+$, 71 (15), 61 (6), 59 (9), 58 (10), 57 (7), 47 (11), 46 (31) $(CH_2S)^+$, 45 (81) $(CHS)^+$, 43 (28), 41 (36). Intensity of the isotopic ions calculated: 6·39% M + 1, 4·76% M + 2; found: 6·24% M + 1, 4·68% M + 2. For $C_5H_{10}OS$ (118·2) calculated: 50·81% C, 8·53% H, 27·12% S; found: 50·54% C, 8·50% H, 27·23% S.

cis-2-*Methyl*-3-*thiolanol* (VIIa): IR spectrum (film, cm^{-1}): 520 w, 567 m, 621 m, 673 m, 695 w, 710 w, 815 m, 850 m, 916 s, 949 s, 985 s, 1024 s, 1070 s, 1140 s, 1174 s, 1210 m, 1260 s, 1302s, 1372 s, 1446 s, 1632 m, 2870 s, 2930 s, 2960 s, 3400 s. IR spectrum (tetrachloromethane, $5 . 10^{-3}$M, cm^{-1}): 3552 (OH bonded), 3629 (OH free), ratio of integrated intensities 1·3 : 1. ^{1}H-NMR spectrum (deuteriochloroform, δ): 4·22 (q, $W = 10·5$ Hz, 1 H, $C_{(3)}$), 3·45 (m, $J_{2,3} = 3·8$ Hz, 1 H, $C_{(2)}$), 2·69–3·21 (m, 2 H, $C_{(5)}$), 1·94–2·37 (m, 2 H, $C_{(4)}$), 1·89 (bs, 1 H, OH), 1·33 (d, $J = 6·8$ Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 118 (86) M^+, 103 (6) $(M - CH_3)^+$, 100 (6) $(M - H_2O)^+$, 90 (33), 85 (23) $(M - CH_3—H_2O)^+$, 74 (55) $(C_3H_6S)^+$, 62 (36), 61 (100) $(C_2H_5S)^+$, 60 (23), 59 (20), 58 (19), 57 (37) $(C_3H_5O)^+$, 46 (8), 45 (18), 43 (9), 41 (26). Intensity of the isotopic ions calculated: 6·39% M + 1, 4·76% M + 2; found: 6·08% M + 1, 4·43% M + 2. For $C_5H_{10}OS$ (118·2) calculated: 50·81% C, 8·53% H, 27·12% S; found: 50·96% C, 8·71% H, 27·05% S.

Cyclisation of *trans*-2-(2-Chloroethyl)-3-methyloxirane (*IVb*) by Potassium Sulphide

The reaction was carried out similarly as described for the *cis*-isomer and afforded 62% yield of a liquid, b.p. 83–86°C/13 Torr, consisting of 11% *IIb* and 89% *VIIb*. Further experiments gave products containing 18% *IIb*, 2% *VIIa*, 80% *VIIb* (gas–liquid chromatography on GE-XE-60, 105°C, R_t 9·6, 14·2, 17·2 min). The mixture was separated by preparative gas–liquid chromatography (GE-XE-60, 150°C, 13–16, 21–27 min) and afforded: erythro-2-(1-*Hydroxyethyl*)*thietane* (IIb): IR spectrum (film, cm^{-1}): 480 m, 510 w, 689 m, 740 m, 805 m, 869 s, 900 s, 963 m, 999 m, 1028 s, 1066 s, 1102 s, 1136 s, 1170 s, 1213 m, 1261 s, 1340 m, 1370 s, 1390 m, 1437 m, 1452 m, 1634 m, 2866 s, 2936 s, 2968 s, 3380 s. IR spectrum (tetrachloromethane, $5 . 10^{-3}$M, cm^{-1}):

3530 (OH bonded), 3624 (OH free), ratio of integrated intensities 2·2 : 1. ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·77 (m, $J_{2,CH-O}$ = 4 Hz, 1 H, CH—O), 3·66 (m, 1 H, $C_{(2)}$), 2·56 to 3·24 (m, 4 H, $C_{(3)}$ and $C_{(4)}$), 2·10 (s, 1 H, OH), 1·10 (d, J = 6·0 Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 118 (72), 75 (10), 74 (100), 73 (62), 71 (14), 61 (7), 59 (7), 58 (7), 57 (6), 47 (9), 46 (27), 45 (63), 43 (20), 41 (30). For the assignment of ions see the *threo*-isomer. Intensity of isotopic ions calculated: 6·39% M + 1, 4·76% M + 2; found: 6·55% M + 1, 4·79% M + 2. For $C_5H_{10}OS$ (118·2) calculated: 50·81% C, 8·53% H, 27·12% S; found: 50·48% C, 8·50% H, 26·88% S.

trans-2-*Methyl*-3-*thiolanol* (VIIb): IR spectrum (film, cm^{-1}): 480 m, 508 w, 525 w, 634 m, 678 m, 715 w, 840 s, 920 s, 953 s, 993 m, 1015 m, 1026 s, 1064 s, 1092 m, 1132 s, 1152 m, 1204 s, 1259 s, 1312 m, 1334 s, 1372 m, 1447 s, 1632 m, 2866 s, 2924 s, 2958 s, 3370 s. IR spectrum (tetrachloromethane, 5 . 10^{-3}M, cm^{-1}): 3555 (OH bonded), 3624 (OH free), ratio of integrated intensities 1 : 4·2. ^{1}H-NMR spectrum (deuteriochloroform, δ): 4·07 (q, W = 11·4 Hz, 1 H, $C_{(3)}$), 3·24 (m, $J_{2,3}$ = 3·5 Hz, 1 H, $C_{(2)}$), 2·93 (t, J = 6·7 Hz, 2 H, $C_{(5)}$), 1·81—2·31 (m, 2 H, $C_{(4)}$), 1·91 (bs, 1 H, OH), 1·26 (d, J = 6·8 Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 118 (90), 103 (7), 100 (7), 90 (34), 85 (25), 74 (55), 62 (40), 61 (100), 60 (21), 58 (19), 59 (21), 57 (26), 46 (8), 45 (17), 43 (8), 41 (26). For assignment of ions see the *cis*-isomer. Intensity of isotopic ions calculated: 6·39% M + 1, 4·76% M + 2; found: 6·06% M + 1, 4·47% M + 2. For $C_5H_{10}OS$ (118·2) calculated: 50·81% C, 8·53% H, 27·12% S; found: 50·71% C, 8·44% H, 26·87% S.

Cyclisation of 3,5-Dichloro-2-pentanol (*I*) by Potassium Sulphide

The cyclisation was carried out according to ref.[7] and afforded a liquid, b.p. 88—90°C/15 Torr, n_D^{20} 1·5244 (ref.[8] b.p. 83—86°C/13 Torr, n_D^{20} 1·5245); yield 53%. IR spectrum (film) was identical with that published in ref.[8]. Ratio of isomers 21% *IIa*, 9% *IIb*, 45% *VIIa*, 25% VIIb (gas–liquid chromatography, GE-XE-60, 105°C, R_t 8·8, 10·1, 15·1, 18·0 min; PEGA, 120°C, R_t 7·8, 8·5, 13·4, 16·2 min). Partial separation by preparative gas–liquid chromatography (GE-XE-60, 106°C, 35—50, 65—82, 90—100 min) afforded:

2-(1-*Hydroxyethyl*)*thietane* (II) (70% *threo*, 30% *erythro*): ^{1}H-NMR spectrum (deuteriochloroform) and mass spectrum were identical with the spectra of thietanes *IIa*, *IIb* obtained by cyclisation of the oxiranes *IVa* and *IVb*. For $C_5H_{10}OS$ (118·2) calculated: 50·81% C, 8·53% H, 27·12% S; found: 51·08% C, 8·64% H, 27·33% S.

cis-2-*Methyl*-3-*thiolanol* (VIIa): ^{1}H-NMR spectrum (deuteriochloroform) and mass spectrum were identical with the spectra of the thiolane *VIIa* from cyclisation of the oxirane *IVa*. For $C_5H_{10}OS$ (118·2) calculated: 50·81% C, 8·53% H, 27·12% S; found: 51·22% C, 8·66% H, 27·40% S. trans-2-*Methyl*-3-*thiolanol* (VIIb): ^{1}H-NMR spectrum (deuteriochloroform) and mass spectrum were identical with the spectra of the thiolane *VIIb* from *IVb*. For $C_5H_{10}OS$ (118·2) calculated: 50·81% C, 8·53% H, 27·12% S; found: 50·49% C, 8·49% H, 28·10% S.

Cyclisation of 1,4-Dichloro-3-pentanol (*V*) by Potassium Sulphide

The cyclisation was carried out in 63% yield analogously to the cyclisation of 3,5-dichloro-2-pentanol. Comparison of the retention times (GE-XE-60, 105°C; PEGA, 120°C) with those of the pure isomers from cyclisations of the oxiranes *IVa*, *IVb* showed that the product contained *threo*- and *erythro*-2-(1-hydroxyethyl)thietane (*IIa* and *IIb*) and *cis*- and *trans*-2-methyl-3-thiolanol (*VIIa* and *VIIb*) in the ratio 16 : 12 : 40 : 32. IR spectrum of this mixture (film) was identical with the spectrum of the product of cyclisation of the alcohol *I*. For $C_5H_{10}OS$ (118·2) calculated: 50·81% C, 8·53% H, 27·12% S; found: 50·51% C, 8·44% H, 27·32% S.

Cyclisation of *cis*-2-(3-Chloropropyl)-3-methyloxirane (*VIa*) by Potassium Sulphide

The reaction was carried out analogously to the cyclisation of the oxirane *IVa*. The procedure differed in that after addition of the oxirane *VIa* the temperature was risen to the boiling point in the course of 90 min and refluxed for one hour. The procedure afforded in 65% yield a liquid, b.p. 116–120°C/15 Torr, consisting of 99% (*VIIIa* + *IXa*) and 1% *VIIIb* (gas–liquid chromatography on GE-XE-60, 105°C, R_t 18·5, 22·0 min). The ratio *VIIIa* : *IXa* was 60 : 40 (poly(ethylene glycol) 600 and sodium 3-aminobenzenesulphonate, 150°C, R_t 9·4, 10·6 min). Compounds *VIIIa* and *IXa* were not separated on GE-XE-60, Apiezon L, Carbowax 20M, Benton 34 + GE-XE-60, OV-17, PEGA, Benton 34 + Carbowax 20M. A single symmetrical peak was also obtained with acetates (PEGA, GE-XE-60, Apiezon K, SE-52). Attempts to separate these compounds by thin-layer chromatography on silica gel using various eluants were also unsuccessful. Separation of the compounds *VIIIa* and *IXa* by preparative gas–liquid chromatography (poly(ethylene glycol) 600 and sodium 3-aminobenzenesulphonate, 120°C, 33–38, 40–44 min) afforded:

threo-2-(1-*Hydroxyethyl*)*thiolane* (VIIIa): IR spectrum (film, cm^{-1}): 400 w, 460 m, 513 m, 538 w, 573 m, 648 m, 705 w, 785 w, 830 s, 842 w, 864 m, 886 s, 906 s, 943 s, 954 s, 968 s, 1012 s, 1020 s, 1047 s, 1065 s, 1109 s, 1128 s, 1152 m, 1119 s, 1199 s, 1230 s, 1263 s, 1309 m, 1324 w, 1371 s, 1348 s, 1440 s, 1634 m, 2864 s, 2938 s, 2940 s, 2968 s, 3420 s. IR spectrum (tetrachloromethane, $5 \cdot 10^{-3}$M, cm^{-1}): 3519 (OH bonded), 3620 (OH free), ratio of integrated intensities 57 : 1. ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·65 (m, $J_{2,CH-O} = 5{\cdot}5$ Hz, 1 H, CH—O), 3·45 (m, 1 H, $C_{(2)}$), 2·82 (t, $J = 6$ Hz, 2 H, $C_{(5)}$), 2·15 (s, 1 H, OH). 1·60–2·14 (m, 4 H, $C_{(3)}$ and $C_{(4)}$), 1·20 (d, $J = 6{\cdot}4$ Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 132 (29) M^+, 117 (8) $(M - CH_3)^+$, 114 (–), 104 (–), 103 (–), 99 (3), 88 (37) $(M - C_2H_4O)^+$, 87 (100) $(M - C_2H_5O)^+$, 75 (–), 61 (2), 60 (24), 57 (2), 45 (24), 43 (9). Intensity of isotopic ions calculated: 7·50% M + 1, 4·83% M + 2; found: 8·40% M + 1, 4·94% M + 2. For $C_6H_{12}OS$ (132·2) calculated: 54·50% C, 9·15% H, 24·25% S; found: 54·22% C, 9·03% H, 23·87% S.

cis-2-*Methyl*-3-*thianol* (IXa): IR spectrum (film, cm^{-1}): 448 w, 524 w, 548 m, 578 w, 630 m, 665 m, 694 w, 710 s, 785 m, 799 s, 829 m, 851 s, 885 s, 895 s, 995 s, 927 s, 1002 s, 1020 s, 1042 s, 1049 m, 1099 s, 1125 m, 1158 s, 1178 m, 1200 m, 1231 w, 1255 s, 1276 s, 1330 m, 1340 m, 1372 s, 1384 s, 1424 m, 1438 s, 1445 s, 1634 w, 2890 s, 2910 s, 2924 s, 2940 s, 2974 s, 3420 s. IR spectrum (tetrachloromethane, $5 \cdot 10^{-3}$M, cm^{-1}): 3518 (OH bonded), 3622 (OH free), ratio of integrated intensities 10 : 1. ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·75 (m, $W = 12$ Hz, 1 H, $C_{(3)}$ equatorial), 3·04 (m, $J_{2,3} = 1$ Hz, $C_{(2)}$), 2·50 (m, 2 H, $C_{(6)}$), 2·14 (bs, 1 H, OH), 1·46–2·03 (m, 4 H, $C_{(4)}$ and $C_{(5)}$), 1·23 (d, $J = 6{\cdot}8$ Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 132 (94) M^+, 117 (2) $(M - CH_3)^+$, 114 (7) $(M - H_2O)^+$, 104 (36), 103 (30) $(M - C_2H_5)^+$, 99 (6), 88 (30) $(M - C_2H_4O)^+$, 87 (8) $(M - C_2H_5O)^+$, 75 (54) $(C_3H_7S)^+$, 61 (100) $(C_2H_5S)^+$, 60 (64), 57 (21) $(C_3H_5O)^+$, 45 (20), 43 (32). Intensity of isotopic ions calculated: 7·50% M + 1, 4·83% M + 2; found: 8·19% M + 1, 4·87% M + 2. For $C_6H_{12}OS$ (132·2) calculated: 54·50% C, 9·15% H, 24·25% S; found: 54·22% C, 9·30% H, 24·05% S.

Cyclisation of *trans*-2-(3-Chloropropyl)-3-methyloxirane (*VIb*) by Potassium Sulphide

The cyclisation was carried out analogously as in the case of the *cis*-isomer, affording in 74% yield a liquid, b.p. 118–122°C/14 Torr, consisting of 2% *VIIIa* + *IXa*, 60% *VIIIb* and 38% *IXb* (GE-XE-60, 105°C, R_t 18·5, 22·0, 30·5 min). Preparative gas–liquid chromatographic separation of the mixture (GE-XE-60, 120°C, 48–64, 72–85 min) afforded:

erythro-2-(1-*Hydroxyethyl*)*thiolane* (VIIIb): IR spectrum (film, cm^{-1}): 465 m, 510 w, 526 w,

574 w, 630 w, 681 m, 725 m, 752 m, 820 w, 838 m, 861 m, 881 s, 934 s, 945 s, 974 s, 1004 s, 1043 s, 1071 s, 1101 m, 1128 s, 1160 w, 1186 s, 1239 m, 1270 s, 1370 s, 1392 s, 1440 s, 1635 m, 2860 s, 2930 s, 2960 s, 3380 s. IR spectrum (tetrachloromethane, $5 . 10^{-3}$M, cm^{-1}): 3528 (OH bonded), 3625 (OH free), ratio of integrated intensities 2·0 : 1. ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·77 (m, $J_{2,CH-O} = 5{\cdot}4$ Hz, 1 H, CH—O), 3·42 (q, 1 H, $C_{(2)}$), 2·81 (m, 2 H, $C_{(5)}$), 2·15 (s, 1 H, OH), 1·72—2·35 (m, 4 H, $C_{(2)}$ and $C_{(3)}$), 1·23 (d, $J = 6{\cdot}4$ Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 132 (35), 117 (5), 114 (1), 104 (1), 103 (1), 99 (3), 88 (42), 87 (100), 75 (1), 61 (4), 60 (21), 57 (2), 45 (20), 43 (8). For assignment of ions see the *threo*-isomer. Intensity of isotopic ions calculated: 7·50% M + 1, 4·83% M + 2; found: 7·56% M + 1, 4·40% M + 2. For $C_6H_{12}OS$ (132·2) calculated: 54·50% C, 9·15% H, 24·25% S; found: 54·16% C, 9·11% H, 24·02% S.

trans-2-*Methyl*-3-*thianol* (IXb): IR spectrum (film, cm^{-1}): 491 w, 535 m, 680 m, 730 m, 803 m, 859 m, 878 s, 904 s, 962 w, 975 m, 1016 s, 1030 s, 1071 m, 1082 m, 1110 m, 1152 m, 1190 m, 1202 m, 1240 s, 1268 m, 1285 m, 1300 w, 1336 w, 1353 m, 1371 m, 1424 s, 1439 s, 1450 s, 1638 m, 2850 m, 2870 m, 2940 s, 2960 m, 3370 s. IR spectrum (tetrachloromethane, $5 . 10^{-3}$M, cm^{-1}): 3524 (OH bonded), 3630 (OH free), ratio of integrated intensities 1 : 4·2. ^{1}H-NMR spectrum (deuteriochloroform, δ): 3·47 (dt, $J_{2,3} = 3{\cdot}8$ Hz, $J_{3,4} = 9{\cdot}9$ Hz, 1 H, $C_{(3)}$ axial), 2·70 (m, 1 H, $C_{(2)}$), 2·49 (t, $J = 4{\cdot}5$ Hz, 2 H, $C_{(6)}$), 1·81—2·25 (m, 4 H, $C_{(4)}$ and $C_{(5)}$), 1·92 (s, 1 H, OH), 1·30 (d, $J = 6{\cdot}7$ Hz, 3 H, CH_3). Mass spectrum, *m/e* (relative intensity, %): 132 (94), 117 (1), 114 (16), 104 (32), 103 (29), 99 (16), 88 (19), 87 (4), 75 (54), 61 (100), 60 (45), 57 (27), 45 (26), 43 (44). For assignment of ions see the *cis*-isomer. Intensity of the isotopic ions calculated: 7·50% M + 1, 4·83 M + 2; found: 7·70% M + 1, 5·25% M + 2. For $C_6H_{12}OS$ (132·2) calculated: 54·50% C, 9·15% H, 24·25% S; found: 54·15% C, 9·01% H, 24·30% S.

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