Stereochemistry of the Methoxyphthioceranes

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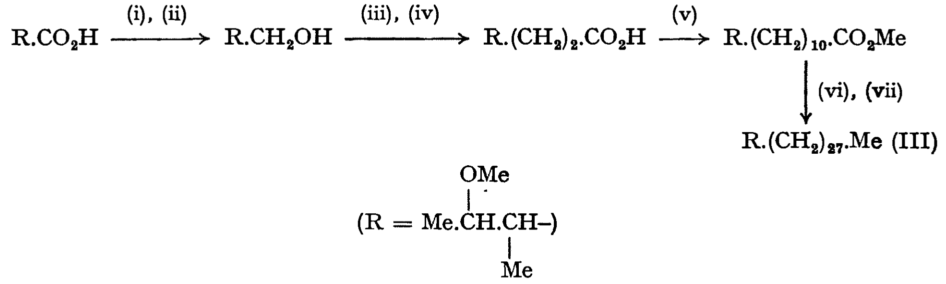
Summary The methoxyphthioceranes derived from phthiocerols A and B are shown to have *erythro*-configuration, thus enabling assignment of absolute configuration to the corresponding asymmetric centres in the phthiocerols.

PHTHIOCEROL consisting mainly of phthiocerol A (I; R = Et) with some (< 5%) phthiocerol B (I; R = Me) was converted by lithium aluminium hydride reduction of the bis-toluene-*p*-sulphonate into the corresponding mixture of methyl ethers. Separation of the mixture by p.l.c. gave 3-methoxyphthiocerane A (II; R = Et) and 2-methoxyphthiocerane B (II; R = Me).



$$R.CO_2H \xrightarrow{\text{(i), (ii)}} R.CH_2OH \xrightarrow{\text{(iii), (iv)}} R.(CH_2)_2.CO_2H \xrightarrow{\text{(v)}} R.(CH_2)_{10}.CO_2Me \xrightarrow{\text{(vi), (vii)}} R.(CH_2)_{27}.Me \text{ (III)}$$

$$(R = Me.\overset{\text{OMe}}{\underset{\text{Me}}{CH}}.CH\text{–})$$

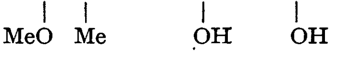
(i) CH_2N_2, (ii) $LiAlH_4$, (iii) toluene-*p*-sulphonyl chloride, (iv) diethyl malonate, (v) mixed electrolysis with methyl hydrogen sebacate, (vi) KOH; aq. EtOH, (vii) mixed electrolysis with nonadecanoic acid.

SCHEME

threo-2-Methoxy-3-methylhentriacontane (III) was prepared from *threo*-3-methoxy-2-methylbutyric acid[1] as outlined in the Scheme.

Examination of the n.m.r. spectra of *threo*-2-methoxy-3-methylhentriacontane and 2-methoxyphthiocerane B shows that the relative configurations of methoxyl and methyl substituents at positions 2 and 3, respectively, are different. The appearance of doublets due to the methyl groups attached to C-2 and C-3 at higher field (τ 8·97 and 9·17 compared with 8·93 and 9·13), and a larger coupling constant for the hydrogen atoms at C-2 and C-3 (5·1, 4·2Hz), is consistent with the assignment of *erythro*-configuration to the mixture of homologues derived from phthiocerol B. Comparison of the n.m.r. spectra of 3-methoxyphthiocerane A with a mixture of *threo*- and *erythro*-3-methoxy-4-methyltridecane, containing predominantly the *threo*-isomer, shows that 3-methoxyphthiocerane A corresponds with the minor component of the mixture, and thus has *erythro*-configuration.

The asymmetric centre bearing the methyl branch at C-4 of phthiocerol A has *S*-configuration[2] and on biogenetic grounds it may be expected that the similar centre at C-3 of phthiocerol B also has *S*-configuration. Hence the centres bearing the methoxyl group at C-3 of phthiocerol A and C-2 of phthiocerol B have *R*-configuration.



$$R.\underset{\text{MeO}}{CH}.\underset{\text{Me}}{CH}.(CH_2)_4.\underset{\text{OH}}{CH}.CH_2.\underset{\text{OH}}{CH}.(CH_2)_n.Me \quad n = 20 \text{ or } 22 \quad \text{(I)}$$

$$R.\underset{\text{MeO}}{CH}.\underset{\text{Me}}{CH}.(CH_2)_m.Me \quad m = 27 \text{ or } 29 \quad \text{(II)}$$

(*Received, April 21st,* 1970; *Com.* 583.)

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[1] K. Maskens and N. Polgar, to be published.
[2] K. Maskens and N. Polgar, *Chem. Comm.*, 1970, 340.