A Novel Rearrangement of *trans*-Tetrahydroabietic Acid in Sulphuric Acid

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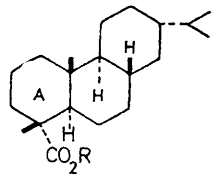
Summary In concentrated sulphuric acid at 0° all-*trans*-tetrahydroabietic acid (I) has been shown to rearrange to optically inactive 7-(1,1-dimethyltetradecahydrophenanthryl)dimethylacetic acid (III).

Dissolution of all-*trans*-tetrahydroabietic acid (I) (shown to contain 11% of its 13-epimer by g.l.c. of its methyl ester)[1] in concentrated sulphuric acid at 0° led, not unexpectedly, to decarbonylation.[2] However, 70—80% of the product was acidic, contained no starting material, and on purification afforded *inter alia* an acid, $C_{20}H_{24}O_2$, m.p. 212—214°, in >10% yield, which was optically inactive (no c.d.) and is shown to have structure (III).† The n.m.r. spectrum of the acid (III) showed no >CHMe signals and the ^{13}C n.m.r. spectrum of its methyl ester, unlike that of the ester (II) which showed resonances assigned to the 19- and 20-methyl groups at δ 16·6 and 14·6 respectively, contained no signals above 20·15, indicating that steric compression of the methyl groups attached to ring A in (II) had been relieved.[3]

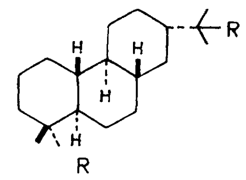
Degradation of the acid (III) by the sequence[4] (IV) → (V) → (VI) → (VII) + (VIII), followed by ozonolysis of the olefin (VIII), gave the ketone (IX), ν_{max} 1709 cm^{-1}, no c.d., and rigorously established the structure of the side chain.

Mild dehydrogenation of the acid (III) over Pd-C gave retene (identified by m.p., u.v. and n.m.r. spectra, and as its picrate) and simonellite (X) identified by comparison with an authentic specimen.[5] Hence the structure of the acid, without reference to stereochemistry, is completely established as (III).

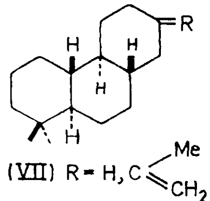
When the rearrangement of tetrahydroabietic acid was carried out in D_2SO_4, the acid (III) was polydeuteriated, indicating that the mechanism is non-concerted and probably involves a series of equilibrating intermediate carbonium ions.[6]



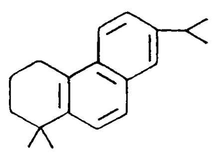
(I) R = H
(II) R = Me



(III) CO_2H
(IV) CON_3
(V) NCO
(VI) NHMe



(VII) $R = H, C\begin{smallmatrix} \diagup Me \\ \diagdown CH_2 \end{smallmatrix}$
(VIII) $R = CMe_2$
(IX) R = O



(X)

The loss of optical activity during the rearrangement requires a symmetrical intermediate and a possible mechan-

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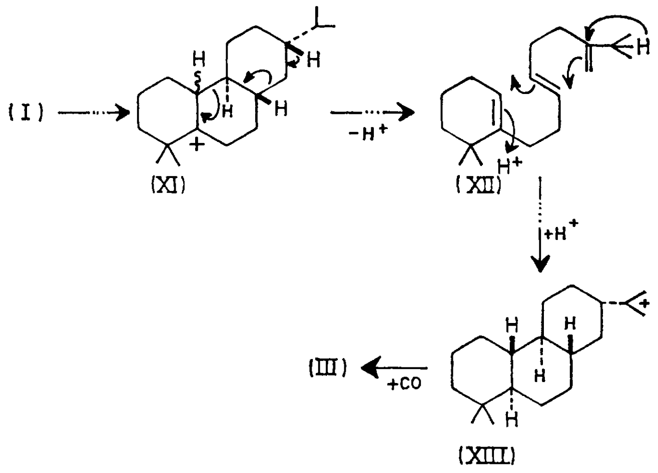
† Structures (III)—(IX) and (XIII) represent racemates.



Scheme

ism is shown in the Scheme. Decarbonylation of the acid (I) affords a carbonium ion at C-4 which rearranges, probably by either (a) a 1,3-methyl shift[7] and a 1,2-hydride shift or (b) several 1,2-methyl shifts and a 1,3-hydride shift, to give the ion (XI). The latter could ring-open to give the triene (XII); on reprotonation the triene could cyclise to the carbonium ion (XIII), which on carbonylation would afford the acid (III). Since the cyclisation of the triene (XII) would probably be stereospecific and give the all-*trans*-stereochemistry (*cf.* ref. 8), the rearranged acid is tentatively assigned the stereochemistry shown in structure (III) Support for the decarbonylation–recarbonylation process[9] was provided by carrying out the rearrangement of the acid (I) in the presence of ^{14}C-labelled carbon monoxide; the product (III) was found to be highly radioactive.

All new compounds gave satisfactory spectral and analytical data.

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