(++)-SYLVETERPIN AND m-CINEOLE

As a prelude to our study on the stereochemistry of sylvetepins, we required pure samples of (±)-sylvetepins I, X = OH) and m-cineole (II).

Two optically inactive sylvetepins, m.p. 94° and 127° designated respectively as cis- and trans-carveterpin are known.1-3 Of these, the lower melting modification was prepared by sulphuric acid catalysed hydration of dihydrocarvostereol (III),1,2 and the other form, from trans-carvostereol dihydrobromide (I, X = Br) by treatment with silver acetate and subsequent hydrolysis of the diacetate by alcoholic potash.1-3

Concerning m-cineole, Perkin and Tattersall noted its formation during the reaction between methyl magnesium iodide and ethyl cyclohexanone-3-carboxylate. The incomplete study of the action of 15% aq. oxalic acid on sylvetepineol, viz., a mixture of m-menthenols (III) and (IV) by Haworth, Perkin and Wallach apparently suggested the feasibility of exploiting this raw material for securing m-cineole. Kuczynski obtained the oxide by refluxing (-)-cis-sylvetepin, m.p. 75° [pure sample melts at 84° (unpublished result)] with 5% aq. oxalic acid.

On the whole, there is no guarantee to the homogeneity of the sylvetepins and m-cineole referred to in literature.

Stirring of (±)-sylvetereol dihydrochloride (I, X = Cl) (17 g) with 2% aq. sodium hydroxide (850 ml) at 70-75° during 5 hr afforded crude carveterpineol (14.3%, m.p. 75°) which by the use of tlc [Kiesel-G-plate; ethyl acetate/n-hexane/n-butanol (1:2:1); detection by vanillin in conc. sulphuric acid] showed the presence of two components. Upon repeated fractional precipitation from benzene/petroleum ether (40-60°), the mixture was resolved into pure tlc (as above) terpineol; cis 0.25%, R, 0.76; trans 2.4%, R, 0.66; their melting points coincided with literature values.1-3

The preparation of the terpines from (±)-sylvetereol dihydrochloride is novel. When sylvetereol (50 g), b.p. 90-92°/5 mm, (a)25 +46-70° (CHCl3, c 1.0), n20 1.4782 was refluxed for 5 hr with 15% aq. oxalic acid (500 ml), dehydration occurred and pure [g]luc (column SE-30, temp. 125°), single peak; tlc as above in benzene/acetone (8:2), single spot; R, 0.86 m-cineole was obtained (5.4%). The structure of m-cineole as (II) is established for the first time by spectral data. Ir. (neat) spectrum disclosed bands at 2915 and 2955 cm-1 (≥C-H), 1455 cm-1 (≥C=H), 1355 and 1365 cm-1 [≥C(CH3)2, 1075 and 1140 cm-1 (≥C-O-C ≤) and 890 cm-1 τ (CH2) ring] and n.m.r. (60 MHz. CCl4) spectrum showed signals at τ 8.7 (s, 3H, CH3), 8.8 and 8.85 (s, 6H, gem-dimethyl), and 7.6-8.5 (complex m, 9H, 4×CH2, CH). Satisfactory elemental analyses were obtained for the compounds reported here.

In the above discussion we have retained the cis-trans configuration of the sylvetepins as in literature.


OXIDATION OF FLUOREN-9-OLS

BY Cr (VI)

The oxidation of a number of secondary alcohols by Cr(VI) has been studied in recent times.1 Conflicting views on the mechanism of these reactions have been expressed especially regarding the nature of the loss of the secondary hydrogen.2 We have now chosen an interesting series of substrates, namely, fluoren-9-ol and its substituted derivatives. In continuation of our earlier work,3 we are now investigating thoroughly the kinetics of these reactions. The kinetics of the oxidation of fluorenyl by Cr(VI) have been reported to be complicated.4
However, the oxidation of fluoren-9-ols are clean exhibiting a total order of two (Fig. 1) being first with respect to each one of the reactants (Table I).

![Graph showing log (k) vs. t(seconds)]

**Table I**

<table>
<thead>
<tr>
<th>[Fluoren-9-ol]</th>
<th>[CrO₂]</th>
<th>k₃ x 10⁴ sec⁻¹</th>
<th>k₆ x 10³ sec⁻¹</th>
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<tr>
<td>0.0500 M</td>
<td>0.008002 M</td>
<td>...</td>
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<td>0.002100</td>
<td>1.88</td>
<td>1.85</td>
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<tr>
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<td>0.002100</td>
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<td>0.004121</td>
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<td>0.02500</td>
<td>0.006005</td>
<td>4.64</td>
<td>1.86</td>
</tr>
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</table>

* Litre mole⁻¹ sec⁻¹.

A plot of log k against σₑₑₑ yields a ρ value of −0.786 (correlation coefficient = 0.9670) (σₑₑₑ values were employed since substituents at the 2 position are meta related to the reaction centre). This probably indicates the formation of an electron-deficient carbon centre in the rate-limiting step due to the cleavage of the C-H bond. Small negative ρ values of this order have been obtained in the Cr(VI) oxidations of p-substituted a-phenyl ethanolols (ρ = −1.01), para-substituted toluenes (ρ = −1.2), diaryl carbinols (ρ = −0.54), and para-substituted mandelic acids (ρ = −1.51).

The definite rate benefit with increasing concentration of acetic acid in the medium [e.g., k₂ (litre mole⁻¹ sec⁻¹) values at 55°C in 70-30, 80-20 and 90-10 acetic acid-water mixtures are 9.44 x 10⁻³, 18.9 x 10⁻³ and 39.8 x 10⁻³ respectively] is in conformity with the observations on other systems. The energy of activation for the oxidation of fluoren-9-ol by Cr(VI) in 80-20 (% v/v) acetic acid-water mixture is 13.73 k cals per mole and the entropy is −24.3 e.u.

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