Perester Oxidation and NBS-Bromination of α-Pinene
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α-Pinene is reported to give, on copper catalyzed perester oxidation, a monobenzate the structure of which was not determined. We repeated the reaction and found that a mixture of alcohols were formed, from which two alcohols, trans-verbenol, I, (30%) and trans-pinocarveol, III, (19%) were obtained in a pure form by column chromatography. A third fraction (9%) was a mixture of myrtenol, IV, (major), cis- and trans-verbenol, II and I, and a fourth hydroxylic compound which had arisen via a skeletal rearrangement. The yields were calculated as percent of the crude alcohol fraction (80-100°C/10 mm) which amounted to 30% based upon α-pinene. The products were identified by comparison with authentic material (myrtenol, trans-pinocarveol) and published NMR data (cis- and trans-verbenol) and trans-pinocarveol). The accepted radical mechanism for the reaction accounts for the products formed.

\[
\begin{align*}
\text{R^+CH_2} \\
\text{I, R, R'' = H; R' = OH} \\
\text{II, R', R'' = H; R = OH} \\
\text{IV, R', R'' = H; R'' = OH} \\
\text{V, R', R'' = H; R'' = Br}
\end{align*}
\]

NBS-Bromination of α-pinene is reported to give a monobromo derivative in a rather vigorous reaction which, however, in our hands proceeded sluggishly. Distillation of the product gave a fraction, b.p. 55-75°C/9 mm, 50%, which apart from some pinene contained at least 6 components in substantial amounts, four of which were separated by preparative GLC. Fraction 1 (11%) was identified as trans-p-cymene, VI by using spectral data and by comparison with authentic material. Fraction 2 (7%), Mw. 216/218, 1:1 (mass spectrographically), is probably fenchyl bromide, VII. The NMR spectrum is closely related to the spectrum of fenchyl alcohol and is not in agreement with the pinane or camphane skeletal. Fraction 3 (48%) consisted of bornyl bromide, VIII, proved by comparison with authentic material. The structure of the compound in fraction 4 (28%) was proved to be myrtenyl bromide, V, using spectral data. No perbenzyl bromide, I, R' = Br, could be detected. Myrtenyl bromide is formed via allylic bromination; the fenchyl and bornyl bromides arise via skeletal rearrangement induced by the addition of hydrogen bromide.

Experimental. Perester oxidation of α-pinene. t-Butyl perbenzoate (4.0 g, 21 mmol) was added over a period of 30 min to a stirred mixture of α-pinene (7.0 g, 51 mmol), [α]_D = +34°, and CuBr (40 mg, 0.035 mmol) at 110°C under nitrogen. After 4 h at this temperature all perester had reacted. The mixture was extracted with sodium carbonate (3 x 50 ml, 2 M) and hydrolyzed with methanolic potassium hydroxide (15 ml, 3 M) for 18 h at 25°C. The free alcohols were precipitated with water, separated and distilled, 1.0 g, 30%, b.p. 80-100°C/10 mm. The distillate was chromatographed on silica with isopropyl ether-petroleum ether, 15:85, as eluent and three fairly well separated main fractions were collected. The first fraction (19%, calculated as per cent of the distillate) is trans-pinocarveol which was gas chromatographically pure; IR: 3610, 3360-3500 cm⁻¹, OH; 3072, 1645, 899 cm⁻¹, C=CH₂; NMR: δ = 4.94 (t), J = 1.0 cps, 1 H, and δ = 4.75 (d), J = 1.0 cps, 1 H, C=CH₂; δ = 4.34 (d, broad), J = 6.8 cps, CHOHOH; δ = 2.65-1.6 (m), 6H+OH; δ = 1.25 (s) and 0.84 (a), 2 CH₃. The NMR spectrum of a sample (impure) synthesized according to Schenek et al. showed the same peaks.

The main component of the second fraction, 9%, is myrtenol, NMR: δ = 5.41 (m), 1 H; δ = 3.89 (m) CH₃OH; δ = 1.31 (s) and 0.85 (a) 2 CH₃. Inspection of the NMR spectrum revealed the presence of trans-verbenol and also small amounts of cis-verbenol. The third fraction, 28%, is trans-verbenol, [α]_D = +72° (c = 1.0, CHCl₃, lit. [α]_D = -124° from pure

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Crystal Data of Some Succinylcholine Salts

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As a part of an investigation of compounds acting as neuromuscular blocking agents, the following crystallographic data have been obtained.

The unit cell parameters have been determined from precession films (MoKα, λ=0.7107 Å) and the estimated uncertainties are 0.2% for the axes and 0.2–0.3° for the angles. The crystal structures of these salts are being studied. In the following the symbol Suc-chol^+ is used for the succinylcholinium ion,

\[
\text{Suc-chol}^+ \rightarrow \begin{array}{c}
\text{H}_2\text{C} \\
\text{O} \\
\text{C} \rightarrow \text{O} \rightarrow \text{CH}_2 \rightarrow \text{CH}_2 \rightarrow \text{N(CH}_3)_\text{2} \\
\end{array} \\
\]

\[\text{Suc-chol}^+, \text{2I}^-\]

Colourless crystals from a water-ethanol solution. M.p. 250–255°C (decomp.).

\[a=12.9_\text{A}, \quad b=8.24_\text{A}, \quad c=9.65_\text{A}, \quad \beta=98.0°\]

\[\eta_{\text{obs}}. 1.76 \text{ g/cm}^3, \quad \eta_{\text{calc}}. 1.778 \text{ g/cm}^3, \quad Z=2, \quad \text{Space group P2_1}.\]

\[\text{Suc-chol perchlorate, Suc-chol}^+, 2\text{ClO}_4^-\]. Colourless crystals from a 50% ethanol solution. M.p. 267–267.5°C. A pronounced tendency to twin-formation was observed.

\[a=6.53_\text{A}, \quad b=13.6_\text{A}, \quad c=12.6_\text{A}, \quad \beta=93.0°\]

\[\eta_{\text{obs}}. 1.43 \text{ g/cm}^3, \quad \eta_{\text{calc}}. 1.444 \text{ g/cm}^3, \quad Z=2, \quad \text{Space group P2_1/c, Molecular symmetry 1}.\]

\[\text{Suc-chol picrate, Suc-chol}^+, 2(\text{NO}_3)_2\text{C}_2\text{H}_5\text{O}^-\]. Yellow needles from a water solution. M.p. 168.5–159°C.

\[a=11.0_\text{A}, \quad b=7.09_\text{A}, \quad c=11.2_\text{A}, \quad \alpha=101.7°, \quad \beta=108.9°, \quad \gamma=94.8°\]

\[\eta_{\text{obs}}. 1.51 \text{ g/cm}^3, \quad \eta_{\text{calc}}. 1.528 \text{ g/cm}^3, \quad Z=1, \quad \text{Space group P1 or P1'}.\]

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