The Synthesis of dl-Hinokione Methyl Ether

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Hinokione has been isolated from the heartwood of several conifers and its structure has recently been shown to be VIII (R = H).

A synthesis of the dl-form of hinokione methyl ether (R = CH₃) has been carried out as indicated in the following scheme:

Succinylation of 2-isopropylphenol methyl ether gave the keto-acid I, m.p. 133–135°, which furnished a deep red 2,4-dinitrophenylhydrazone, m.p. 85–88°. The keto-acid was reduced by Clemmensen’s method to the acid II, m.p. 31–34°. The corresponding acid chloride when treated with aluminium chloride furnished the a-tetralone III, b.p. 136–138°/1 mm, $\lambda_{\text{max}}$ 263 m$\mu$ (e, 12 700) and 225 (19 700), $\nu_{\text{co}}$ 1 675 cm$^{-1}$ (film), further characterised as the deep red dinitrophenylhydrazone, m.p. 198–200°. The a-tetralone III reacted with methyl magnesium iodide giving a product that on treatment with potassium hydrogen sulphate underwent dehydration to yield the dihydronaphthalene IV, b.p. 101–104°/0.3 mm. IV was epoxidised with perbenzoic acid and the product isomerised with dilute sulphuric acid to the $\beta$-tetralone V, b.p. 111–116°/0.1 mm, $\nu_{\text{co}}$ 1 715 cm$^{-1}$ (film) which gave a crystalline semicarbazone, m.p. 184–187°.

The $\beta$-tetralone V was condensed with $\beta$-chlorodiethyl ketone in the presence of sodium hydride to give the $\alpha,\beta$-unsaturated ketone VI, m.p. 92–94°, $\nu_{\text{co}}$ 1 665 and $\nu_{\text{cc}}$ 1 623 cm$^{-1}$, $\lambda_{\text{max}}$ 287 m$\mu$ (e 4 160), 279 (4 720), 230 (16 000) and 247 (17 100), giving a red 2,4-dinitrophenylhydrazone, m.p. 225–228°. Methylation of VI with methyl iodide and potassium t-butoxide led to the ketone VII, m.p. 92–94°, $\nu_{\text{co}}$ 1 712 and $\nu_{\text{cc}}$ 1 668 cm$^{-1}$, (2,4-dinitrophenylhydrazone, m.p. 212–214°), which was hydrogenated in ethanol in the presence of Pd/C to dl-hinokione methyl ether VIII (R = CH₃), m.p. 119–121°, (2,4-dinitrophenylhydrazone, m.p. 215–218°). The I.R. spectra of the synthetic and the natural hinokione methyl ether (in carbon tetrachloride) were superimposable.

The U.V. spectra were taken in 95 % ethanol solution and the I.R. spectra in carbon tetrachloride unless otherwise specified. Satisfactory analyses were obtained for all the compounds described.

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