Tetrahedron Letters No. 21 pp. 9-11, 1960. Pergamon Press Ltd. Printed in Great Britain

HYDROBORATION OF β-PINENE

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(Received 25 July 1960)

WE wish to correct our earlier[2] tentative assignment of the cis or "iso" configuration to the l-myrtanol obtained by hydroboration of β-pinene at 130° with pyridine-borane followed by oxidation of the myrtanyl borane with hydrogen peroxide and also to clarify recent reports by Dulou and Chretien-Bessiere[3] that myrtanol (methylol group trans to the gem dimethyl group) was obtained using diborane as the hydroborating agent and by Brown[4] that this reaction yielded isomyrtanol.

We have now found that myrtanol, isomyrtanol or any desired mixture of the two can be obtained by the anti-Markownikoff hydration of β-pinene by proper control of the hydroboration conditions.

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[2] J.C. Braun and G.S. Fisher, Abstracts of Papers, Southeastern Regional Meeting of Local ACS Sections, Gainesville, Florida Dic. 1958; FLACS, 12, No. 3, 46 (1958).

[3] R. Dulou and Y. Chretien-Bessiere, Bull.Soc.Chim.Fr. 1362 (1959).

[4] H.C. Brown, Southwestern Regional Meeting of Local ACS Sections, Baton Rouge, La., 1959.

Dupont and Zacharewicz[5] prepared *l*-myrtanol, (d_0^0 = 0.9858, n_D^{20} = 1.4898, $[\alpha]_D$ = 26°) by sodium reduction of myrtenol of unspecified rotation and *l*-isomyrtanol (d_{20}^{20} = 0.9803, n_D^{21} = 1.4925 $[\alpha]_D$ = -24.5°) by catalytic hydrogenation of *l*-myrtenol (from *l*-β-pinene). Assignment of the *cis* configuration to isomyrtanol was confirmed by Eigenmann and Arnold.[6] Authentic samples of *l*-myrtanol and *l*-isomyrtanol were prepared by the published methods[5,6] and purified by gas-liquid chromatography (GLC) for determination of their infrared spectra. Emergence times of the two isomers differed only slightly but there were marked differences in their spectra in the 9-11μ region. When the alcohol obtained via the reaction of pyridine-borane with β-pinene[2] was purified in the same way it was found to be identical to the authentic *l*-myrtanol. Hence, the tentative identification[2] as *l*-isomyrtanol, based on physical properties and analogy to the formation of *l*-isopinocampheol [m.p. 52-3°, $[\alpha]_D$ = -33° (c = 10 benzene)] from d-pinene under the same conditions,[2] was incorrect.

The following properties were found for *l*-myrtanol and *l*-isomyrtanol purified by GLC: *l*-myrtanol, d_4^{25} = 0.971, n_D^{25} 1.4863, $[\alpha]_D$ = -28° (C, 14.7 *p*-cymene), major I.R. peaks at 9.45 and 9.85 μ, *l*-isomyrtanol, d_4^{25} = 0.971, n_D^{25} = 1.4881, $[\alpha]_D$ = -18° (C, 17.5 *p*-cymene), major I.R. peaks at 9.6 (broad) and 9.95 μ.

Using Brown's general procedure[7] for hydroboration with gaseous diborane and subsequent oxidation, all at low temperature, substantially pure

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[5] G. Dupont and W. Zacharewicz, *C.R. Acad. Sci., Paris* **199**, 365 (1934).

[6] G.W. Eigenmann and R.T. Arnold, *J.Amer.Chem.Soc.* **81**, 3440 (1959).

[7] H.C. Brown and G. Zweifel, *J.Amer.Chem.Soc.* **81**, 247 (1959).

isomyrtanol was obtained. Dulou's procedure[3] differed from that of Brown chiefly in that the temperature of hydroboration was not controlled, the solvent was removed "with as little heat as possible," and the oxidation with hydrogen peroxide was carried out in refluxing ethanol. Using this technique isomyrtanol of high purity was obtained again. However, substantially pure myrtanol was obtained when the solvent was removed after the hydroboration step by slow distillation over a period of seven hours allowing the pot temperature to rise to 140°. Samples of the myrtanyl borane withdrawn at intervals during the solvent removal and oxidized with hydrogen peroxide yielded mixtures of isomyrtanol and myrtanol.

Hence, in the case of β-pinene the hydroboration at about room temperature occurs stereospcifically from the less hindered side of the molecule, i.e. trans to the bulky gem dimethyl group, to yield the thermodynamically unstable isomyrtanyl borane as predicted.[2,7] However, subsequent heating of the borane converts it almost quantitatively to the more stable myrtanyl borane.

Positional isomerization of the alkyl boranes at about 140° is well known, but this is apparently the first case of stereoisomerization without migration of the borane group. Work is under way to explore the scope and mechanism of this isomerization to the thermodynamically stable borane.