

DITERPENOIDS: XIX "RUZICKA'S HYDROCARBON"^{*}

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(Received in UK 6 May 1968; accepted for publication 26 June 1968)

Recent communication (1,2,3) on manool-derived diterpenoids prompt us to report a further extensive rearrangement in this field.

Ruzicka (4) in 1931 described the formation of a hydrocarbon $C_{20}H_{32}$ from sclareol (I) with β -naphthalenesulphonic acid at 190°C. The product was distilled off molten sodium. The structure (II) assigned (5) to this hydrocarbon is inconsistent with the properties of the compound, in that structure (II) is unlikely to be the stable end-product of a carbonium ion rearrangement, and structure (II) would certainly react with molten sodium. Furthermore the optical rotation of the compound is inconsistent (6) with structure (II).

Repetition of Ruzicka's work using either sclareol (I), manool (III), biformene (IV) or cis-abienol (V), gave the hydrocarbon mixture obtained by Ruzicka, b.p. 108°/0.07 mm, $[\alpha]_D -6^\circ$, n_D^{17} 1.5224, d_4^{17} 0.940 [literature values (4): b.p. 125-8°/0.2 mm, $[\alpha]_D -14^\circ$, n_D^{17} 1.5217, d_4^{17} 0.9388]. Distillation off sodium gave a cleaner product, but was not necessary in the formation of the product. Gas chromatography gave one major peak and numerous minor ones.

The major fraction was isolated by chromatography over alumina and silver nitrate-silica gel, b.p. 120°/0.1 mm, $[\alpha]_D + 2.3^\circ$, ca. 99% one peak by gas chromatography. The product, $C_{20}H_{30}$, had aromatic bands in the infrared and had an ultraviolet spectrum characteristic of a pentasubstituted benzene (264, 270, 276 $m\mu$; ϵ 260, 370, 275). The p.m.r. spectrum indicated an isopropyl group, two saturated methyl groups, two methyl groups and three additional protons benzylic to an aromatic ring, and a lone aromatic proton. Structure (X) is proposed for the hydrocarbon.

* Diterpenoids: XVIII. R.M. Carman, H.C. Deeth, R.A. Marty, K. Mori and M. Matsui, Tetrahedron Letters, in the press.