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THE BASE CATALYSED REARRANGEMENT OF *cis*- AND *trans*-β-OCIMENE TO *trans*-4-*trans*-6-ALLOOCIMENE

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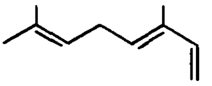
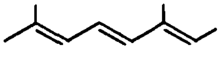
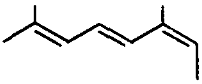
Abstract—The base catalysed rearrangement of *cis*- and *trans*-β-ocimene gives exclusively *trans*-4-*trans*-6-alloocimene. *trans*-β-Ocimene has been isolated from neroli bigarade oil.

DURING an investigation of the composition of neroli bigarade oil by gas chromatography, it was observed that saponification of the oil significantly reduced the intensity of one of the hydrocarbon peaks. The substance responsible for this peak was isolated by a combination of column and preparative gas chromatography and shown to be identical in IR, UV. and NMR spectra[1] with *trans*-β-ocimene (I).


I


II


III


IV

When an alcoholic solution of *trans*-β-ocimene was heated to reflux with KOH, a more complex UV spectrum developed. The position and intensity of the absorption bands suggested that a conjugated triene system was being generated. The reaction gave a single product with IR spectrum identical to that reported for *trans*-4-*trans*-6-alloocimene (III).[2] The presence of strong absorption at 954 cm^{-1} (CH out-of-plane deformation in *trans* CH:CH) and the absence of any absorption in the 730–665 cm^{-1} region (CH out-of-plane deformation in *cis* CH:CH) are in accord with a *trans*-configuration at the 4,5 double bond. The UV absorption spectrum with maxima at 264, 272·5 and 283 mμ agrees with the literature data for *trans*, *trans*-alloocimene.[3]

The NMR spectrum in CCl_4 showed signals at τ 8·29 (doublet, 3H, C-8 protons, $J \sim$ Hz), 8·22 (singlet, 9H, two terminal vinyl Me groups and 6-Me group), 4·50 (quartet, 1H, C-7 proton, $J \sim$ Hz) and 4·22 (doublet, 1H, C-3 proton, $J \sim 11$ Hz). This last signal was revealed more clearly when the quartet at τ 4·50 was spin decoupled. The rest of the olefinic signals (2H) gave a complex multiplet.

cis-β-Ocimene (II) behaved analogously to the *trans*-isomer when subjected to the reaction with KOH and yielded *trans, trans*-alloocimene as major product. Unlike the thermal rearrangement of *cis*-β-ocimene,[4] no *trans*-4-*cis*-6-alloocimene (IV) appears to be formed under the reaction conditions. The stability of the *trans, cis*-isomer to these conditions excludes the possibility that its absence from the reaction product is due to subsequent isomerisation to the *trans, trans*-isomer.

EXPERIMENTAL

Routine GLC was carried out on a Perkin–Elmer F11 gas chromatograph fitted with a flame ionisation detector and a 4 m × 1/8 in column of LAC-2R-446 on Chromosorb W (15:85 w/w) at 120° with a N_2 flow rate of 40 ml/min. Temperature programming at the rate of 3°/min from 80° to 160° was used for the essential oils. Preparative gas chromatography was carried out on a Perkin–Elmer F21 gas chromatograph using LAC-2R-446 on Chromosorb P (20:80 w/w) at 95° as stationary phase. The IR spectra were recorded as liquid films on a Hilger & Watts H 800 spectrophotometer, the UV spectra were measured in EtOH with a Uvispek spectrophotometer, and the NMR spectra were obtained in CCl_4 at 100 MHz on a Varian HA 100 spectrometer with TMS as internal standard.

trans-β-Ocimene (I). (a) *Italian neroli bigarade* oil (10 g) was adsorbed on a column (36 × 3 cm) of silica gel prepared from a slurry with light petroleum, b.p. below 40°. Elution with light petroleum gave the hydrocarbon fraction (3·8 g). GLC indicated the presence of 3 major components. The component with the longest retention time was isolated by preparative gas chromatography. The UV, IR and NMR spectra corresponded to the data published for *trans*-β-ocimene.[1]

(b) The monoterpene fraction was flash distilled from English distilled oil of opoponax (Bush Boake Allen) (100 g) at 0·2 mm on a steam bath and redistilled to yield *trans*-β-Ocimene (45 g), b.p. 29–30°/0·1 mm: n_D^{22} 1·4850; λ_{max} 232 mμ (ε 26,750).

Base catalysed isomerisations. trans-β-Ocimene (15 g) ex opopanax was heated to reflux in EtOH (15 ml) with KOH (3 g) for 14 hr. After cooling, the product was diluted with light petroleum, b.p. 40–60 . (30 ml) and washed with water. Evaporation of the light petroleum and distillation of the resulting oil gave *trans-4-trans*-6-alloocimene (III) (12·7 g), b.p. 68°/0·1 mm; n_D^{23} 1·5425; λ_{max} 264 (ε 33,070), 272·5 (ε 42,800), and 283 mμ (ε 33,500). The IR spectrum was identical with the published spectrum.[2]

cis-β-Ocimene[5] (0·17 g) was reacted similarly with KOH (0·1 g) in EtOH (5 ml). The product (0·15 g) gave a single peak by GLC and was identical in IR and UV spectra with *trans, trans*-alloocimene.

trans-4-*cis*-6-alloocimene[3] was recovered unchanged after being subjected to the isomerisation conditions.

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REFERENCES

[1] G. Ohloff, J. Seibl and E. Kovats, *Liebigs Ann. Chem.* **675**, 83 (1964)
[2] B. M. Mitzner, E. T. Theimer and S. K. Freeman, *Appl. Spectrosc.* **19**, 169 (1965)
[3] K. J. Crowley, *J. Org. Chem.* **33**, 3679 (1968)
[4] J. Wolinsky, B. Chollar and M. D. Baird, *J. Amer. Chem. Soc.* **84**, 2775 (1962)
[5] B. M. Mitzner, S. Lemberg and E. T. Theimer, *Canad. J. Chem.* **44**, 1090 (1966)