A Novel Reaction of Carene

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IN the course of our investigations of simple terpenes we have re-examined the catalytic hydrogenation of (+)-Δ^3-carene (I), $[\alpha]_D^{20}$ + 15·4°, n_D^{20} 1·4726. Reduced in ethanol over palladised charcoal at 20° in 1 atmosphere of hydrogen it afforded approximately equal amounts of (−)-*cis*-carane (II) and 1,1,4-trimethylcycloheptane (III). However, at 96° in propionic acid, 2 moles of hydrogen were absorbed and (III) was formed exclusively, although Δ^3-carene is unaffected by propionic acid alone at the temperature stated.

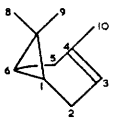
Hydrogenation of (+)-Δ^3-carene in ethanol over platinised charcoal at 20° and 100 atmospheres of hydrogen gave principally (−)-*cis*-carane with

less than 2·5% of (III). So far we have not found *trans*-carane in any of our hydrogenation products.

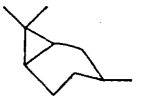
(−)-*cis*-Carane and 1,1,4-trimethylcycloheptane were purified by preparative g.l.c. and then gave satisfactory elemental analyses. The former, $[\alpha]_D^{20}$ − 20·7°, n_D^{20} 1·4548, gave a single peak on three columns which readily resolved *cis*- and *trans-m*- and -*p*-menthanes and pinanes. Its structure was assigned by analogy with the catalytic hydrogenation products of α-pinene[1] and from consideration of its n.m.r. spectrum, for which we are indebted to Dr. E. F. Mooney. The spectrum showed resonance at τ 9·02 (singlet, three protons, 9-methyl), 9·07 (singlet, three protons, 8-methyl), 9·18 (doublet, J = 5·5 c./sec., three protons, 10-methyl) and 9·2—9·8 (multiplet, two protons, cyclopropane protons).

1,1,4-Trimethylcycloheptane (III), n_D^{20} 1·4414, had identical physical properties and g.l.c. patterns with those given by a specimen prepared[2] from eucarvone, and its n.m.r. spectrum showed absorption at τ 9·12 (singlet, 8- and 9-methyl protons) with superimposed doublet (J = 5·5 c./sec., 10-methyl protons) and no cyclopropane proton absorption.

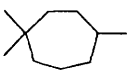
Formation of (III) from Δ^3-carene may involve 1,4-hydrogen addition to an intermediate, *e.g.* Δ^2- or Δ^4-carene. This possibility, for which we have some evidence, is being currently investigated.



(I)



(II)



(III)

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[1] Unpublished results from this laboratory.
[2] J. R. B. Campbell, A. M. Islam, and R. A. Raphael, *J. Chem. Soc.*, 1956, 4096.