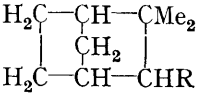
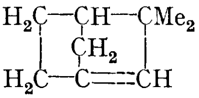
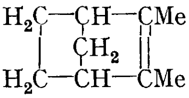
386. *Snitter's Camphenilene.*

By G. GRATTON and J. L. SIMONSEN.

BY the dehydration of camphenilol (I) or by the removal of hydrogen chloride from camphenilyl chloride (I), Jagelki (*Ber.*, 1899, **32**, 1503) and Hintikka and Komppa (*Annalen*, 1912, **387**, 292) prepared a hydrocarbon, camphenilene, to which the structure (II) was given. Meerwein's suggestion (*Annalen*, 1914, **405**, 135) that camphenilene is identical with santene (III) was shown to be correct by Komppa and Hintikka (*Bull. Soc. chim.*, 1917, **21**, 14). They found, however, that the hydrocarbon was not homogeneous and contained probably some camphenilene, since on ozonolysis it gave, in addition to 1 : 3-diacetyl*cyclo*pentane, a small quantity of a ketonic aldehyde.


(I, R = OH or Cl.)


(II.)


(III.)

Recently Snitter (*Bull. Inst. Pin.*, 1933, 209) has prepared this hydrocarbon, which he describes as a crystalline solid, m. p. 26·5°, from both camphenilol and camphenilyl chloride. On the evidence of the Raman spectrum he concludes that it is nearly pure camphenilene contaminated with 2—5% of apobornylene but free from santene. Since this conclusion, if correct, would be of considerable theoretical importance, in that it would provide the first exception to the well-established Bredt rule,* we have re-examined the hydrocarbon.

By the elimination of hydrogen chloride from camphenilyl chloride we have prepared a hydrocarbon which agrees closely in its physical properties with santene, Komppa and Hintikka's and Snitter's hydrocarbons :

	Santene.	K. and H.	S.	G. and S.
B. p.	140—141°/770 mm.	138—142°	140—142°	138—141°/765 mm.
$d_{20°}^{20°}$	0·863	$d_{17°}^{17°}$ 0·870	$d_{21°}^{21°}$ 0·8699	$d_{25°}^{25°}$ 0·862
$n_{\mathrm{D}}^{20°}$	1·46658	$n_{\mathrm{D}}^{17°}$ 1·46758	$n_{\mathrm{D}}^{21°}$ 1·4676	$n_{\mathrm{D}}^{20°}$ 1·4667

Oxidation of the hydrocarbon with ozone showed that it was, contrary to Snitter's statement, far from homogeneous, but, in agreement with Komppa and Hintikka, consisted essentially of santene. The main product of the oxidation was 1 : 3-diacetyl*cyclo*pentane, and in addition to acidic products, formaldehyde, a ketone, $C_8H_{12}O$, characterised

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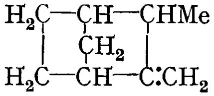
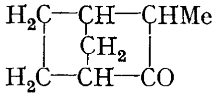
* The very unstable ketone, carvopinone, is a possible exception to the rule.

by its crystalline 2 : 4-*dinitrophenylhydrazone*, m. p. 114—115°, and a saturated hydrocarbon, C_9H_{14}, m. p. 42°, were obtained. The saturated hydrocarbon was undoubtedly apocyclene, the formation of which was not unexpected and does not call for comment. The isolation of formaldehyde and of the ketone $C_8H_{12}O$ suggest the presence of (IV) in the hydrocarbon mixture, the ketone being methylnorcamphor (V).

(IV.)





(V.)

Comparison of the 2 : 4-dinitrophenylhydrazone referred to above with *methylnorcamphor*-2 : 4-*dinitrophenylhydrazone*, m. p. 116—117°, prepared from methylnorcamphor (Diels and Alder, *Annalen*, 1928, **460**, 120; 1931, **486**, 202) showed that the two hydrazones were not identical, but it is not improbable that the oxidation ketone was the stereoisomeric form of methylnorcamphor. We obtained no evidence of the presence of the ketonic aldehyde mentioned by Komppa and Hintikka. The acidic products of the oxidation were found to be a complex mixture; the presence of *iso*butyric acid was established, but ketonic acids were almost entirely absent. The formation of *iso*butyric acid suggests contamination with monocyclic hydrocarbons, and this would be anticipated if any camphenilene were formed during the dehalogenation. We suggest the possibility that Snitter's hydrocarbon, m. p. 26·5°, consisted essentially of apocyclene, m. p. 42°, since the melting point of this hydrocarbon is much depressed by traces of impurities. In the present state of our knowledge it would appear to us to be dangerous to base the determination of structure solely on the evidence of the Raman spectrum, unsupported by confirmation by standard chemical methods.

EXPERIMENTAL.

The hydrocarbon was prepared by the action of freshly distilled diethylaniline on camphenilyl chloride. A portion of the chloride, b. p. 190—194°/755 mm. (Found: Cl, 21·9. $C_9H_{15}Cl$ requires Cl, 22·3%), was not acted upon by diethylaniline; its constitution was not determined. Prior to oxidation the hydrocarbon was distilled over sodium. The hydrocarbon (4 g.) in carbon tetrachloride (15 c.c.) was treated with ozone at 0°; formaldehyde evolved with the issuing gases was identified by its derivative with dimedone, m. p. and mixed m. p. 186—187°. On completion of the oxidation the solvent was removed in a vacuum, and the ozonide decomposed by boiling with water. After addition of sodium carbonate the residual oil was extracted with ether, the ether evaporated, and the residue distilled in steam. The volatile portion was redissolved in ether, the solution dried and evaporated, and the residual oil fractionated through a Widmer column, three fractions being obtained: (i) b. p. 45°/20 mm., (ii) 76—78°/15 mm., and (iii) 127—130°/15 mm. Fraction (i), which crystallised, was redistilled over sodium; it then had b. p. 138°/763 mm., m. p. 42°, gave no colour with tetranitromethane, and was probably apocyclene (Found: C, 88·3; H, 11·5. Calc. for C_9H_{14}: C, 88·5; H, 11·5%). Fraction (ii), which was insufficient in quantity for purification, gave a yellow 2 : 4-dinitrophenylhydrazone; this was not homogeneous, but after repeated crystallisation from alcohol a *hydrazone* was obtained in orange needles, m. p. 114—115° (Found: C, 55·1; H, 5·4. $C_{14}H_{16}O_4N_4$ requires C, 55·3; H, 5·3%). On admixture with *methylnorcamphor*-2 : 4-*dinitrophenylhydrazone*, orange-coloured needles, m. p. 116—117° (Found: C, 55·1; H, 5·1%), the m. p. was depressed to 94°. Fraction (iii) was identified as 1 : 3-diacetyl*cyclo*pentane by the preparation of the disemicarbazone, decomp. 216°, and by oxidation with sodium hypobromite to *trans*-*cyclo*pentane-1 : 3-dicarboxylic acid, which was converted through the anhydride into the *cis*-acid, m. p. 120° (Semmler and Bartelt, *Ber.*, 1908, **41**, 387).

The sodium carbonate solution from which the neutral oil had been separated was acidified and, after saturation of the solution with ammonium sulphate, repeatedly extracted with ether; evaporation of the solvent left a viscid oil, which gave only a faint turbidity with 2 : 4-dinitrophenylhydrazine. The acid was esterified with diazomethane, and the methyl ester distilled under diminished pressure. A small fraction, b. p. below 115°/19 mm., was hydrolysed, and the resulting acid converted into the *p*-phenylphenacyl ester. This partly solidified; the solid, after repeated crystallisation from alcohol, had m. p. 85°, and 85—87° in admixture with *p*-

phenylphenacyl *iso*butyrate. The acids present in the higher-boiling fractions could not be identified.

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