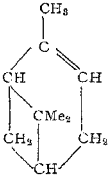
SYNTHETICAL EXPERIMENTS IN THE PINANE GROUP, PART VII.

Total synthesis of Verbenone : A new total synthesis of *a*- and *β*-Pinenes.

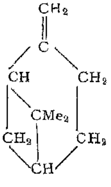
By P. C. Guha and P. L. Narasimha Rao.

The synthesis of *a*- and *β*- pinenes (I and II) could not be said to have been definitely achieved until very recently ; the claims of a complete synthesis of pinocamphone[1] by Ruzicka and Trebler and thus of the pinenes[2] were dependent on the supposed conversion of *a*-campholenic acid to 1-pinonic acid hy Tiemann[3] which has been proved to be erroneous.[4] The formation of *β*-pinene from linalyl chloride claimed by Wanin and Tschernojarowa[5] represents a singularly unique type of reaction and lacks in full experimental details and in confirmatory evidence.

Conversion of pinane[11] via. its chlorination-products into pinenes by G. Bonnet[6] can be regarded as the first total synthesis of *a*-and *β*-



(I)



(II)

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[1] *Helv. Chim. Acta.*, 1920, **3**, 756 ; 1921, **4**, 666 ; 1924, **7**, 489.

[2] Cf. Dupont and Zacharewicz, *Compt. rend.*, 1935, **200**, 759.

[3] *Ber.*, 1896, **29**, 3015.

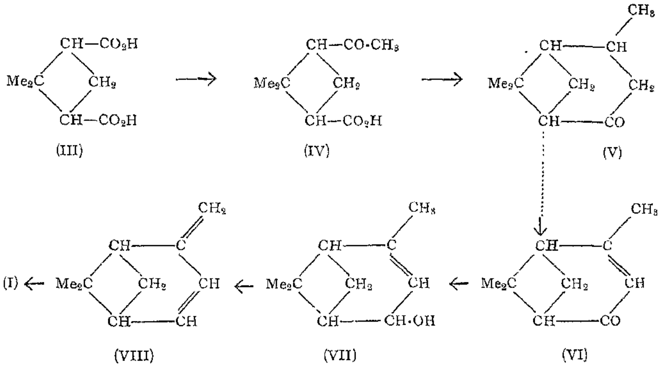
[4] Komppa and Beckmann, *Ber.*, 1936, **69B**, 2783.

[5] Wanin and Tschernojarowa, *Chem. J. Ser. A. J. allg. Chem. (Russ. Chimitscheski Shurnal. Sser. A. Shurnal Obschtschei Chimii)*, 1937, **7**, (69), 885 ; *Chem. Zentr.*, 1937, II, 1187.

[6] G. Bonnet, *Bull. Inst. Pin.*, 1938, 217-32, 241-56 ; *Ibid.*, 1939, 1-12.

pinenes. Conversion of verbenone into pinocamphone reported recently in a note by Komppa and his collaborators[7]* constitutes another total synthesis of the pinenes.

Starting from cyanacetic ester, Kerr[8] synthesised *trans*-norpinic acid which was converted into the *cis*-form (III) by Shoppee and Simonsen.[9] From the anhydride of the acid Guha and Ganapathi[10] synthesised *cis*-pinononic acid (IV). Komppa and Klami[11] have synthesised verbanone (V) starting from *cis*-pinononic acid.



Blumann and Zeitshel[12] converted verbenone into dihydroverbenene via. verbenol (VII) and verbenene (VIII). Although

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[7] Komppa, Klami and Kuvaja, *Naturwiss*, 1939, **12,** 197.

* While this work was almost completed (cf. Guha and Narasimha Rao, *Science and Culture,* 1939, **5,** (i), 64), Komppa and his collaborators published the note[7] describing their total synthesis of *α*-pinene.

[8] Kerr, *J. Amer. Chem. Soc.*, 1929, **51,** 614.

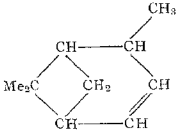
[9] Shoppee and Simonsen, *J. Soc. Chem. Ind.*, 1929, **48**, 730.

[10] Guha and Ganapathi, *Ber.*, 1936, **69,** 1185.
cf. Guha and P.V.A. Raman, *Appendix to Ann. Reports of Indian Inst. Sci.*, 1939. p. 56.

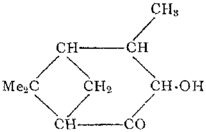
[11] Komppa and Klami, *Ber.*, 1937, **70,** 788.

[12] Blumann and Zeitshel, *Ber.*, 1921, **54,** 887.

dihydroverbenene was assumed by them to be δ-pinene (IX), it has been proved to be α-pinene by Ruzicka.[13] Thus for a complete synthesis of α-pinene it only remains that verbanone should be converted into verbenone. This has now been effected in a single step by the action of selenium dioxide upon verbanone, and constitutes a new total synthesis of pinene and the first total synthesis of verbenone.



(IX)



(X)

The mechanism of this interesting conversion can be explained on the assumption that the active methylene group of (V) gets first oxidised to (CH.OH) giving rise to the intermediate compound (X) which then loses a molecule of water to give rise to verbenone (VI). This is in accordance with the studies of Lydia Monti[14] on the mechanism of oxidation of organic compounds by selenium dioxide.

Some of the experiments of Blumann and Zeitshel[2] have now been repeated with verbenene purified and freed from α-pinene and it has been found that α-pinene is definitely formed during the reduction of verbenene by sodium and alcohol. Moreover, contrary to the statements of Blumann and Zeitshel that dihydroverbenene did not give any pinonic acid on oxidation[15], the latter has now been isolated as its semicarbazone from the products of oxidation of dihydroverbenene.

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[13] Ruzicka and Trebler, *Helv. Chim. Acta.*, 1924, **7**, 489.

[14] *Gazz. Chim. ital.*, 1938, **68**, 608.

[15] Simonsen, *The Terpenes*, Vol. **11**, p. 185.

EXPERIMENTAL.

Pure *dl*-verbanone was prepared by reduction of verbenone (from *dl*-pinene by autoxidation) with PtO and hydrogen according to the method of Komppa and Klami[11] and purified by distillation after treatment with dilute solution of permanganate as described by Wienhaus and Schumm[16].

Conversion of verbanone into verbenone (VI).—A mixture of verbanone (22.4 g.), alcohol (96%. 50 c.c.) and selenium dioxide (13.6 g.) was heated under reflux for 12 hours. The alcohol was distilled off (the last traces in vacuum on water-bath) and the residue subjected to prolonged steam-distillation. The distillate, after extraction with ether and drying was fractionated as follows: (i) b.p., below 80-85°/10 mm., 2 g.; (ii) b.p., 90-110°/10 mm., 3.5 g.; (iii) b.p., 110-125°/10 mm., 10 g.

The fraction (ii) was treated with semicarbazide hydrochloride and sodium acetate in alcoholic solution and the resulting semi-carbazone after four crystallisations (0.8 g.) melted at 180-82° and remained undepressed when taken admixed with a genuine sample of verbenone semicarbazone. (Found: N, 19.8. $C_{11}H_{17}ON_3$ requires N, 20.3 per cent.).

Isolation of pinonic acid from the products of oxidation of dihydroverbenene (a-pinene). Verbenene was purified *via.* its dibromo compound according to the method of Blumann and Zeitshel[12]. *dl*-Verbenene, boiled at 155-58°/689 mm.; n_D^{25}, 1.4965. By repeating their reduction of verbenene, (30 g.) with sodium and alcohol, pure dihydroverbenene, b.p.152-154°/670 mm., n_D^{25}, 1.4624 (8 g.) was obtained after two fractionations.

On oxidation with potassium permanganate according to the recent and improved method[17] of oxidation of α-pinene into pinonic acid, a thick gummy acid was obtained from which a very small quantity of

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[16] *Annalen*, 1924, **439**, 20.

[17] Slawinski and Zacharewicz, *Roczniki Chem.*, 1934, **14**, 213.

crystals slowly deposited. It was then dissolved in alcohol and treated with a solution of semicarbazide hydrochloride and sodium acetate. After a day characteristic crystalline lumps of pinonic acid semicarbazone separated out, m.p. 206-7°, which remained undepressed when taken admixed with an authentic specimen of *dl*-pinonic acid semicarbazone.

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Printed at the Hosali Power Press, Ulsoor, Bangalore, by D. N. Hosali, Proprietor.