SYNTHETICAL EXPERIMENTS IN THE PINANE GROUP,
PART VII.

Total synthesis of Verbenone: A new total synthesis of
\( \alpha \)- and \( \beta \)- Pinenes.


The synthesis of \( \alpha \)- and \( \beta \)- 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
\( \alpha \)-campholenic acid to 1-pinonic acid by Tiemann\(^3\) which has been
proved to be erroneous.\(^4\) The formation of \( \beta \)- pinene from linalyl
chloride claimed by Wanin and Tschernojarova\(^5\) represents a singularly
unique type of reaction and lacks in full experimental details and in
confirmatory evidence.

Conversion of pinane\(^6\) via its chlorination-products into pinenes
by G. Bonnet\(^6\) can be regarded as the first total synthesis of \( \alpha \)-and \( \beta \)-

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3 Ber., 1896, 29, 3015.
4 Komppa and Beckmann, Ber., 1936, 69B, 2783.
Chmitcheski Shrurnal. Sser. A. Shrurnal Obschtschei Chimii), 1937,
pinenes. Conversion of verbenone into pinocamphone reported recently in a note by Komppa and his collaborators constitutes another total synthesis of the pinenes.

Starting from cyanacetic ester, Kerr synthesized trans-norpinic acid which was converted into the cis-form (III) by Shoppee and Simonsen. From the anhydride of the acid Guha and Ganapathi synthesized cis-pinonic acid (IV). Komppa and Klami have synthesised verbanone (V) starting from cis-pinonic acid.

Blumann and Zeitshel converted verbenone into dihydro-verbenene via verbenol (VII) and verbenene (VIII). Although

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7 Komppa, Klami and Kuvaaja, Naturwiss., 1939, 12, 197.
8 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 describing their total synthesis of α-pinene.
10 Guha and Ganapathi, Ber., 1936, 69, 1185.
12 Komppa and Klami, Ber., 1937, 70, 788.
13 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. 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.

The mechanism of this interesting conversion can be explained on the assumption that the active methylene group of (V) gets first oxidised to (CH₂.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 on the mechanism of oxidation of organic compounds by selenium dioxide.

Some of the experiments of Blumann and Zeitshel 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, the latter has now been isolated as its semicarbazone from the products of oxidation of dihydroverbenene.

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15 Simonsen, The Terpenes, Vol. 11, p. 185.
EXPERIMENTAL.

Pure *dl*-verbenone was prepared by reduction of verbenone (from *dl*-pinene by autoxidation) with PtO and hydrogen according to the method of Komppa and Klami11 and purified by distillation after treatment with dilute solution of permanganate as described by Wienhaus and Schumm16.

Converter of verbenone into verbenone (VI).—A mixture of verbenone (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. C₁₃H₁₈ON₃ 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 Zeitshel12. *dl*-Verbenene, boiled at 155-58°/689 mm.; *n*₂⁰, 1.4965. By repeating their reduction of verbenene, (30 g.) with sodium and alcohol, pure dihydroverbenene, b.p.152-154°/670 mm., *n*₂⁰, 1.4624 (8 g.) was obtained after two fractionations.

On oxidation with potassium permanganate according to the recent and improved method17 of oxidation of *a*-pinene into pinonic acid, a thick gummy acid was obtained from which a very small quantity of

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

Department of Pure and Applied Chemistry,
Indian Institute of Science,
Bangalore