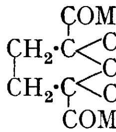
289. *Experiments on the Synthesis of Santene and its Derivatives. Part I.*

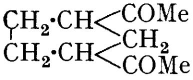
By Lalit M. Mohunta and Jnanendra N. Rây.

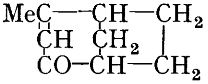
The constitution of the hydrocarbon santene (C_9H_{14}) occurring in *Santalum album* L. has been established by Semmler and Bartelt (*Ber.*, 1907, **40**, 4595; 1908, **41**, 128, 389, 867). It is the only substance known to disobey the isoprene rule, and it has been suggested that it is formed naturally from teresantalic acid by a Wagner transformation after hydration and decarboxylation. The earlier syntheses of santene (cf. Hintikka and Komppa, *Annalen*, 1912, **387**, 292; Ruzicka and Liebl, *Helv. Chim. Acta*, 1923, **6**, 271) all involve the Wagner rearrangement, but recently a direct synthesis was effected by Diels and Alder (*Annalen*, 1931, **486**, 205) by dehydration of γ-santenol, from methylmagnesium iodide and 6-methyl-*nor*camphor; this, however, is not unambiguous, for dehydration may take place in an alternative direction *via* a tricyclene. A simple synthesis, however, is now described.

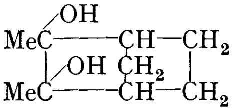
The disodio-derivative of ethyl $\alpha\alpha'$-diacetyladipate (I) condenses with methylene iodide in toluene solution to give the ester (II), which was directly hydrolysed to 1 : 3-diacetyl*cyclo*pentane (III), identical (disemicarbazone) with the diketone prepared by Semmler and Bartelt (*loc. cit.*) by ozonolysis of santene. The dicyclic ketone (IV) was always formed simultaneously and was identical with the substance prepared by the same authors from the diketone (III) by reaction with sodium ethoxide; it gives a *semicarbazidosemicarbazone*, formed by the addition of a second molecule of the reagent at the double bond (cf. Rupe and Schlochoff, *Ber.*, 1903, **36**, 2796, 4377).

$CH_3\cdot CO\cdot CH(CO_2Et)\cdot(CH_2)_2\cdot CH(CO_2Et)\cdot CO\cdot CH_3$ (I.)


(II.)


(III.)


(IV.)


(V.)

The ketone (III), when reduced in moist ethyl acetate solution with aluminium amalgam, furnished santene glycol (V), identical with the substance prepared by oxidation of santene with potassium permanganate solution. The diketone (III) reacted vigorously with an excess of phenylhydrazine in acetic acid at 100° with copious evolution of nitrogen to give santene in amount too small for the preparation of a solid derivative (cf. Perkin, Rây, and Robinson, J., 1927, 2096).

EXPERIMENTAL.

Ethyl αα′-diacetyladipate was prepared according to Perkin (J., 1890, **57**, 215), but purification *via* the imido-derivative was wasteful. The crude product was subjected to rapid steam distillation for 25—30 mins., the residue extracted thrice with ether, the extract washed with sodium bicarbonate solution, dried (sodium sulphate; and in a vacuum over sulphuric acid for 12 hrs.), and rapidly distilled; b. p. 155—160°/4—6 mm.; yield 20%.

Ethyl 1 : 3-*Diacetyl*cyclo*pentane*-1 : 3-*dicarboxylate* (II).—To a solution of sodium (1·6 g.) in dry alcohol (22 c.c.), the foregoing ester (10 g.) and toluene (70 c.c.) were added, and the mixture boiled under reflux with methylene iodide (9·3 g.) for 5 hrs. (the bromide can be used as well). After removal of the solvents, the residue was heated in a vacuum at 100° for a few minutes, water added, and the mixture extracted with a large volume of ether. The oily residue from ether (10 g.) was used directly for the next stage, since it decomposed on distillation in a vacuum.

The oil (7·5 g.) was gradually added with shaking to potassium hydroxide solution (28 c.c. of 10%), and shaking was continued for 2 hrs. with occasional cooling. After extraction with a large volume of ether, an oil (3·5 g.) was obtained; b. p. 125—130°/10 mm., 95—98°/2 mm. The disemicarbazone (Found : N, 31·4. Calc. for $C_{11}H_{20}O_2N_6$: N, 31·4%) had m. p. 216°, not depressed on admixture with an authentic specimen (Semmler and Bartelt, *loc. cit.*, give m. p. 216°).

If the alkaline mixture in the above hydrolysis was allowed to become hot (or if it was boiled with alcohol under reflux), the ketone (IV) was obtained; b. p. 100—101°/9 mm.; $n_D^{33°}$ 1·5038 (Semmler and Bartelt give $n_D^{20°}$ 1·5139). With semicarbazide, it gave a *semicarbazidosemicarbazone*, m. p. 205° (Semmler and Bartelt give 205°, but record no analysis) (Found : C, 49·1; H, 7·6; N, 31·7. $C_{11}H_{20}O_2N_6$ requires C, 49·3; H, 7·4; N, 31·4%), depressed on admixture with the above semicarbazone.

Santene Glycol (V).—The diketone (III) (1·0 g.), dissolved in moist ethyl acetate (100 c.c.), was reduced with amalgamated aluminium (from 5 g. of Al) for 12 hrs., and the solution filtered from aluminium oxide and evaporated, giving a viscous substance, b. p. 134—137°/9—10 mm. This crystallised in thick prisms on long standing in a vacuum, m. p. 191—192° (Found : C, 69·0; H, 10·4. Calc. for $C_9H_{16}O_2$: C, 69·2; H, 10·2%), and revealed no difference when compared with the glycol prepared from natural sources.

In this reduction, variable results were obtained, which we ascribe to the fact that the ketone (III) may be a *trans*-compound, because on oxidation with sodium hypobromite it affords *trans*-*cyclo*pentane-1 : 3-dicarboxylic acid (cf. Semmler and Bartelt, *loc. cit.*). However, its conversion into the dicyclic ketone (IV) by means of sodium ethoxide suggests that it and the *cis*-isomeride are readily interconvertible.

UNIVERSITY OF THE PANJAB, LAHORE.

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