

STUDIES IN NAPHTHALENE SERIES

Part II. The Synthesis of the *Trans*-form of *Trans*-decalin-2-carboxy-3-acetic Acid

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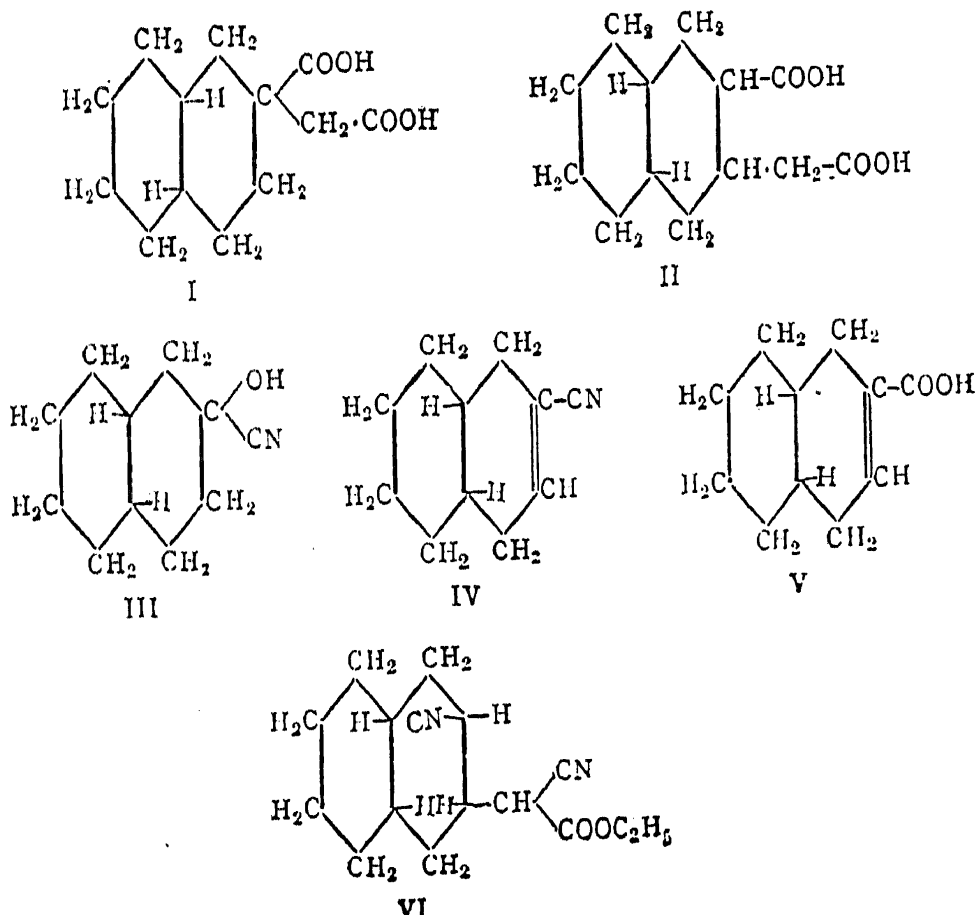
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Received November 6, 1939

THE preparation and properties of the stereo-isomeric *trans*-decalin-1-carboxy-1-acetic acid (I) have been fully studied by Hückel and Wiebke¹ and Rao.² Our final objective was to study the preparation of *cis* and *trans* forms of *trans*-decalin-2-carboxy-3-acetic acid (II) and to compare their properties, but as the chances of resuming our interrupted work are uncertain, we have thought it necessary to record our results so far obtained.

Trans- β -decalone-cyanohydrin (III) which was prepared in a pure form by the bisulphite method, was smoothly dehydrated to the unsaturated nitrile by thionyl chloride in pyridine solution. This nitrile (IV) was proved to be 2-cyano- Δ -2:3-*trans*-octalin as it was quantitatively oxidised by alkaline potassium permanganate to cyclohexane-1:2-diacetic acid.³ Concentrated hydrochloric acid hydrolysed the nitrile to *trans*- Δ -2:3-octalin-2-carboxylic acid (V), as oxidation with alkaline potassium permanganate gave cyclohexane-1:2-diacetic acid.



The addition of ethyl sodio-cyanoacetate to the unsaturated nitrile did not proceed smoothly and a poor yield of ethyl *trans*-decalin-*trans*-2-cyano-3-cyanoacetate (VI) was obtained. As the investigations of Hückel and Goth⁴ as well as Cook and Linstead⁵ have shown that such Michael condensations usually lead to *trans* addition, the cyano-acetic ester (VI) must have the *trans*-configuration. Prolonged hydrolysis with concentrated hydrochloric acid gave the *trans* form of *trans*-decalin-2-carboxy-3-acetic acid (II).

Experimental

Trans- β -decalone was prepared by the method of Rao (*loc. cit.*). *Trans*- β -decalone-cyanohydrin (III). To a suspension of the sodium bisulphite compound prepared from decalone (60 g.) and sodium bisulphite (42 g.), potassium cyanide solution (34 g. in 75 c.c. H₂O) was slowly added with vigorous shaking, and cooling under the tap. The oily cyanohydrin began to separate out immediately, and completed after standing for 12 hours. The liquid was extracted with ether, dried, and the solvent removed. The residue, after the addition of 2 or 3 drops of concentrated sulphuric acid, distilled constantly at 113°/6 mm. (yield 65–70 per cent.). (Found : C, 73.5 ; H, 9.5 ; C₁₁H₁₇ON requires C, 73.7 ; H, 9.5 per cent.)

Trans-2-cyano- Δ -2 : 3-octalin.—To the solution of the cyano-hydrin (36 g.) in dry pyridine (32 c.c.), thionyl chloride (36 g.) was gradually added at 0°. After allowing the mixture to remain at the room temperature for three hours, it was heated on the water-bath under reflux for four hours, and decomposed with ice-cold water. The separated oil was extracted with ether, the ethereal layer thoroughly washed with alkali, dried, and distilled when a liquid boiling at 145°/6 mm. was obtained (yield 20 g.). (Found : C, 81.9 ; H, 9.3 ; C₁₁H₁₅N requires C, 82.0 ; H, 9.3 per cent.)

This nitrile which has a peculiar odour did not absorb bromine and was not reduced by aluminium amalgam.

Oxidation of the nitrile to cyclohexane-1 : 2-diacetic acid.—A suspension of the nitrile (1 g.) in water (50 c.c.) was shaken up with 5 per cent. alkaline potassium permanganate till the solution was no longer decolourised. The alkaline solution, on being acidified with concentrated hydrochloric acid, gave an acid which was identified by m.p. (164°) and mixed m.p. as cyclohexane-1 : 2-diacetic acid.

Trans- Δ -2 : 3-octalin-2-carboxylic acid (V).—The mixture of the nitrile (5 g.) and concentrated hydrochloric acid (25 c.c.) was heated on sand-bath under reflux for 12 hours, the cooled mixture extracted with ether, and the

acidic material removed with alkali. On acidifying the alkaline solution, the solid acid crystallised from alcohol in small plates, m.p. 146°. (Found: C, 73.0; H, 9.0; $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.9 per cent.)

Its chloroform solution did not absorb bromine readily. The alkaline solution was shaken up with a dilute solution of potassium permanganate till a pink colour was produced. Acidification of the alkaline solution with concentrated hydrochloric acid gave an acid, m.p. 164°, which was identified as cyclohexane-1:2-diacetic acid.

Trans-decalin-trans-2-carboxy-3-acetic acid (II). The unsaturated nitrile (16 g.) was slowly added to a suspension of ethyl sodiocyanoacetate [prepared from sodium (2.3 g.); ethylecyanoacetate (12 g.) and alcohol (35 c.c.)]. Cooled to 0° with constant shaking, and the mixture allowed to stand at the room temperature for 12 hours. After heating on the water-bath for six hours, the mixture was poured into water acidified with dilute hydrochloric acid and the precipitated oil was extracted with ether. The acidic as well as semi-acidic material was extracted from the ethereal solution with 10 per cent. alkali, and was again extracted with ether from the alkaline solution after acidification. The neutral portion consisted mainly of the unreacted nitrile, together with a small amount of ethyl cyanoacetate. The unreacted nitrile was oxidised by alkaline potassium permanganate to cyclohexane-1:2-diacetic acid.

As the addition product (5 g.) showed the tendency to decompose during distillation under the reduced pressure, the crude ester was mixed with concentrated hydrochloric acid (25 c.c.), and the mixture was heated on the sand-bath under reflux for 24 hours. The semi-solid product which appeared on cooling was extracted with ether, and the ethereal solution was thoroughly shaken up with a 5 per cent. sodium carbonate solution. The alkaline solution on being acidified gave a solid which crystallised from benzene in needles, m.p. 214–15°. The benzene mother-liquor, on concentration, gave an impure acid, m.p. 160–80°, which could not be purified. (Found: C, 64.8; H, 8.2; $C_{13}H_{20}O_4$ requires C, 65.0; H, 8.3 per cent.)

We hope to resume this work at the earliest opportunity.

Summary

Trans- Δ -2:3-octalin-2-carboxylic acid and *Trans-Decalin-trans-2-carboxy-3-acetic acid* have been synthesised.

REFERENCES

1. Hückel and Wiebke .. *Ber.*, 1926, 59, 2843.
2. Rao .. *J.*, 1926, 1954.
3. Hückel and Friedrich .. *Annalen*, 1927, 441, 132.
Kandiah .. *J.*, 1931, 935.
4. Hückel and Goth .. *Ber.*, 1925, 58, 447.
5. Cook and Linstead .. *J.*, 1934, 954.