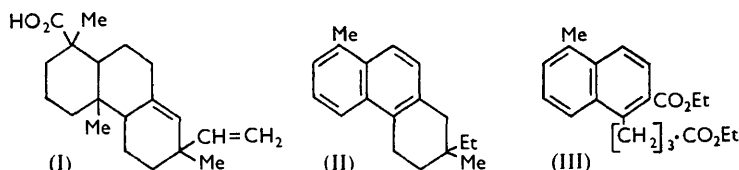


871. Studies in Polycyclic Systems. Part IV.* Synthesis of Some Degradation Products of Dextropimaric Acid and Related Diterpenoids.

By D. NASIPURI and A. C. CHAUDHURI.

The synthesis of two naphthalene derivatives (II and VIII) is described. The former is identical with the trisubstituted naphthalene obtained by partial dehydrogenation^{1,2} of dextropimaric acid and related diterpenoids. The latter (VIII) is found to differ, in its trinitrobenzene derivative, from a hydrocarbon derived from the two isomeric dextropimaric acids and to which this formulation was ascribed.¹

It was shown by Harris and Sanderson¹ that partial dehydrogenation of dextro- or *isodextro*-pimaric acid (I) with palladium-charcoal gave a trisubstituted naphthalene which they formulated as 2-ethyl-1 : 2 : 3 : 4-tetrahydro-2 : 8-dimethylphenanthrene (II) on the basis of its ultraviolet absorption spectra and further dehydrogenation to pimanthrene. The same hydrocarbon, along with pimanthrene, was also isolated by these workers² from the dehydrogenation product of yet another diterpene which they



described as *isodextropimarinal* and identified as cryptopinone (it was, however, established later by Barton, Bruun, and Sørensen³ that cryptopinone was dextropimarinal). The transformation of these diterpenoids into the hydrocarbon is rather curious⁴ and evidently brought about by intramolecular "transfer-hydrogenation" of the vinyl group with partial dehydrogenation of the hydrophenanthrene nucleus. The stability of the hydrocarbon (II) towards further dehydrogenation is expected and recalls the isolation of similar trisubstituted naphthalene derivatives from the dehydrogenation products of methyl tosyl ether.⁵ We now confirm the structure of this hydrocarbon by a rational synthesis as follows.

2-Ethyl-1 : 2 : 3 : 4-tetrahydro-8-methyl-1-oxophenanthrene, prepared from ethyl γ -(2-ethoxycarbonyl-5-methyl-1-naphthyl)butyrate⁶ (III) by the usual procedure of Dieckmann cyclisation, ethylation, and hydrolysis, was alkylated with methyl iodide in the presence of potassium *tert.*-butoxide, to give 2-ethyl-1 : 2 : 3 : 4-tetrahydro-2 : 8-dimethyl-1-oxophenanthrene. Clemmensen reduction of the latter afforded the desired hydrocarbon (II), the identity of which with the C₁₈H₂₂ hydrocarbon derived from the diterpenoids was shown by ultraviolet absorption spectra, a mixed melting point of the trinitrobenzene derivatives, and also by superimposable X-ray diffraction patterns and infrared absorption spectra of these derivatives. It appears, therefore, that the two hydrocarbons isolated from dextropimaric acid and *isodextropimaric* acid are racemic and not the two expected enantiomers differing in the configuration of the quaternary carbon atom. This was also proved by Harris and Sanderson¹ from the absence of optical rotation of the hydrocarbons although the mechanism of racemisation during dehydrogenation is not apparent.

* Part III, Nasipuri, J., 1958, 2734.

¹ Harris and Sanderson, *J. Amer. Chem. Soc.*, 1948, **70**, 2081.

² *Idem, ibid.*, p. 3870.

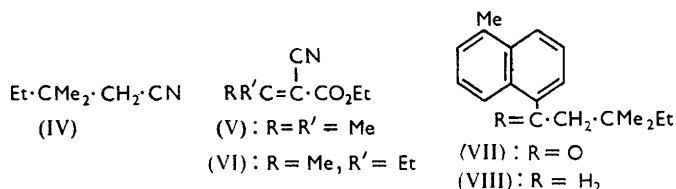
³ Barton, Bruun, and Sørensen, *Acta Chem. Scand.*, 1951, **5**, 1356; and also Sørensen and Bruun, *Acta Chem. Scand.*, 1947, **1**, 112.

⁴ Cf. Harper, *Ann. Reports*, 1948, **45**, 180.

⁵ Short and Wang, *J.*, 1951, 2979.

⁶ Bardhan and Nasipuri, *J.*, 1956, 350.

Harris and Sanderson also derived a second naphthalene hydrocarbon represented by the structure (VIII), from dextro- and *isodextro*-pimaric acid¹ through the successive stages of selective hydrogenation of the vinyl group, ozonolysis of the dihydro-acids, Wolff-Kishner reduction, and dehydrogenation. For the synthesis of this hydrocarbon, we condensed 5-methyl-1-naphthylmagnesium bromide⁷ with $\beta\beta$ -dimethylvaleronitrile (IV). The latter was obtained by controlled hydrolysis of ethyl 2-cyano-3:3-dimethylpentanoate,^{8,9} prepared by the action of either (a) ethylmagnesium bromide on ethyl 2-cyano-3-methylcrotonate (V) or (b) methylmagnesium iodide on ethyl 2-cyano-3-methyl-2-pentenoate (VI). The ketimine hydrochloride, thus formed, was hydrolysed to the ketone (VII) and next converted into the hydrocarbon (VIII) by Martin's modified procedure¹⁰ of Clemmensen reduction. The trinitrobenzene derivative of this hydrocarbon, on crystallisation from ethanol, melted at 113–116° as reported by Harris and Sanderson¹ for their corresponding compound. But on subsequent crystallisations, the melting point rose abruptly and reached a constant value of 141–142°. Reduction of the



ketone (VII) by treatment with a mixture of anhydrous aluminium chloride and lithium aluminium hydride¹¹ gave the same results. Apparently the trinitrobenzene derivative of this synthetic hydrocarbon differs from that of Harris and Sanderson unless we are dealing with a polymorph. On the other hand, the natural trinitrobenzene derivative might well have been impure as judged from the broad melting range. The ultraviolet absorption curves of the hydrocarbons are similar, having an intense band at 228 m μ , characteristic of disubstituted naphthalenes. No sample, however, was available for comparison.

Two other methods of hydrogenation—use of palladium-charcoal in presence of a trace of perchloric acid,¹² and a mixed catalyst of platinum and palladium¹³—failed to reduce the ketone (VII).

EXPERIMENTAL

2-Ethyl-1:2:3:4-tetrahydro-2:8-dimethyl-1-oxophenanthrene.—Ethyl γ -(2-ethoxycarbonyl-5-methyl-1-naphthyl)butyrate (III), m. p. 113°, on Dieckmann cyclisation, ethylation, and hydrolysis as described⁶ for analogous cases, gave *2-ethyl-1:2:3:4-tetrahydro-8-methyl-1-oxophenanthrene*, m. p. 120° (Found: C, 85.5; H, 7.7. $\text{C}_{17}\text{H}_{18}\text{O}$ requires C, 85.7; H, 7.6%). The ketone (5 g.) in dry *tert.*-butyl alcohol (30 ml.) was added to a cooled solution of potassium *tert.*-butoxide prepared from potassium (3 g.) and *tert.*-butyl alcohol (60 ml.) under nitrogen. Methyl iodide (15 ml.) was then added and the mixture was stirred at room temperature for 4 hr. and then left overnight. Next day the solvent was evaporated under reduced pressure, and the *product* isolated in the usual way; it crystallised from methanol in leaflets (3.5 g.), m. p. 61–62° (Found: C, 85.4; H, 8.1. $\text{C}_{18}\text{H}_{20}\text{O}$ requires C, 85.7; H, 7.9%).

2-Ethyl-1:2:3:4-tetrahydro-2:8-dimethylphenanthrene (II).—The preceding ketone (2 g.) was refluxed with amalgamated zinc (10 g.) and concentrated hydrochloric acid (10 ml.) for

⁷ Bardhan, Nasipuri, and Mukherjee, *J.*, 1957, 921.

⁸ Prout, *J. Amer. Chem. Soc.*, 1952, **74**, 5915; also Prout, Huang, Hartman, and Korpics, *ibid.*, 1954, **76**, 1911.

⁹ Birch, *J.*, 1949, 2721.

¹⁰ Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438.

¹¹ Brown and White, *J.*, 1957, 3755.

¹² Rosenmund and Karg, *Ber.*, 1942, **75**, 1850; Johnson, Christiansen, and Ireland, *J. Amer. Chem. Soc.*, 1957, **79**, 1995.

¹³ Koebner and Robinson, *J.*, 1938, 1994.

20 hr. The product on isolation and distillation over sodium in *vacuo* gave the hydrocarbon (II) (1 g.), b. p. 148—150/0.1 mm. (Found: C, 90.6; H, 9.4. Calc. for $C_{18}H_{22}$: C, 90.8; H, 9.2%). The ultraviolet absorption spectra had two intense bands at 232 and 325 μ . The trinitrobenzene derivative crystallised from ethanol in yellow needles, m. p. 123—123.5° (Found: C, 64.4; H, 5.6; N, 9.5. Calc. for $C_{18}H_{22}, C_6H_3O_6N_3$: C, 63.9; H, 5.5; N, 9.3%). It showed no depression in m. p. when mixed with a sample (furnished by Dr. T. F. Sanderson), m. p. 122—123°, derived from the diterpenoids and had identical X-ray diffraction patterns and infrared absorption spectra. The hydrocarbon (II) (0.4 g.) was dehydrogenated with 10% palladium-charcoal¹⁴ (20 mg.) to pimanthrene,¹⁵ m. p. and mixed m. p. 86°.

$\beta\beta$ -Dimethylvaleronitrile (IV).—Ethyl 2-cyano-3:3-dimethylpentanoate, b. p. 115—117°/15 mm., was prepared according to Prout's directions⁸ by the action of ethylmagnesium bromide on ethyl α -cyano- β -methylcrotonate¹⁶ (V) and alternatively by the action of methylmagnesium iodide⁹ on ethyl 2-cyano-3-methylpent-2-enoate¹⁷ (VI) in approximately the same yield (30%). Hydrolysis of the cyano-ester (18.3 g.) by refluxing a solution in potassium hydroxide (10 g.) and ethylene glycol (30 ml.) for 5 hr. gave the nitrile (IV) (9.2 g.), b. p. 164° (Found: C, 75.6; H, 11.8; N, 12.7. $C_7H_{13}N$ requires C, 75.7; H, 11.7; N, 12.6%).

1-Methyl-5- $\beta\beta$ -dimethylvaleryl $naphthalene$ (VII).—A solution of 1-bromo-5-methylnaphthalene (11.1 g.) in ether (35 ml.) was added dropwise to a suspension of magnesium (2.2 g.) in ether (30 ml.), the reaction being initiated by addition of a few drops of ethyl bromide. Dry thiophen-free benzene (40 ml.) was next added and the mixture gently refluxed on the steam-bath for 4 hr. $\beta\beta$ -Dimethylvaleronitrile (9 g.) in benzene (25 ml.) was gradually dropped in and the whole refluxed for 6 hr., cooled, and poured into ice-water containing concentrated hydrochloric acid (25 ml.). The solvent was removed by steam-distillation and the ketimine hydrochloride (10 g.), m. p. 248—250°, was collected by filtration and dried. It was hydrolysed in refluxing water (60 ml.), concentrated hydrochloric acid (30 ml.), and toluene (35 ml.) for 3 hr. After cooling, the mixture was diluted with water, the organic layer was separated, and the aqueous layer once extracted with benzene. The combined organic extract was washed with water, dried, and evaporated at the water-pump, and the residue was distilled to afford the ketone (VII) (9 g.), b. p. 170—172°/1 mm. (Found: C, 84.6; H, 8.8. $C_{18}H_{22}O$ requires C, 85.0; H, 8.7%). It did not give a semicarbazone under ordinary conditions.

Synthesis of the Hydrocarbon (VIII).—(a) A mixture of the ketone (VII) (4 g.), amalgamated zinc (20 g.), concentrated hydrochloric acid (35 ml.), water (15 ml.), toluene (20 ml.), and glacial acetic acid (2 ml.) was refluxed for 30 hr. The product was worked up in the usual way and distilled over sodium, to give an oil (2 g.), b. p. 150—152°/2 mm. (Found: C, 89.7; H, 9.9. Calc. for $C_{18}H_{24}$: C, 90.0; H, 10.0%). The trinitrobenzene derivative crystallised from ethanol in yellow needles, m. p. 113—116°; but after several crystallisations, the m. p. rose to a constant value of 141—142° (Found: C, 63.3; H, 5.7; N, 9.5. Calc. for $C_{18}H_{24}, C_6H_3O_6N_3$: C, 63.6; H, 6.0; N, 9.3%). Harris and Sanderson¹ record m. p. 113—116°.

(b) The ketone (VII) (2 g.) in ether (2 ml.) was slowly added to a cold solution of lithium aluminium hydride (0.52 g.) and anhydrous aluminium chloride (3.7 g.) in dry ether (3 ml.). The mixture was warmed on the steam-bath for 30 min., then cooled, and the excess of the reagent was destroyed by cautious addition of ethyl acetate. The product was taken up in ether, washed with water, and dried, the solvent was removed, and the residue was distilled, to give an oil (1.1 g.), b. p. 152—155°/2 mm. The trinitrobenzene derivative crystallised from ethanol in yellow needles, m. p. 141—142° (Found: C, 63.5; H, 5.8; N, 9.3%).

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¹⁴ Linstead and Thomas, *J.*, 1940, 1127.

¹⁵ Haworth, Letsky, and Mavin, *J.*, 1932, 1784.

¹⁶ Cope, *J. Amer. Chem. Soc.*, 1937, **59**, 2327.

¹⁷ Cope, Hofmann, Wyckoff, and Hardenbergh, *ibid.*, 1941, **63**, 3452.