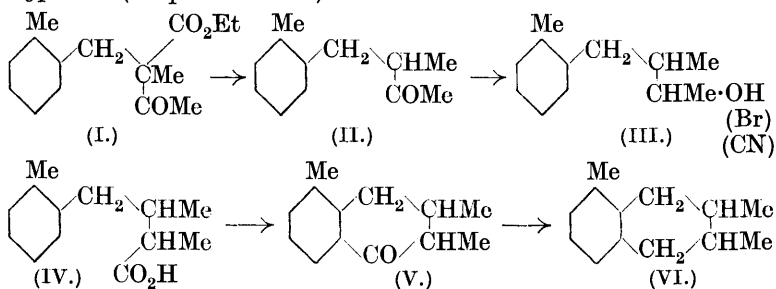


CLXXVI.—*Synthesis of Alkyl Naphthalenes. Part III. 2 : 3 : 5-Trimethylnaphthalene.*

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IN continuation of previous work on the synthesis of alkyl naphthalenes (Harvey, Heilbron, and Wilkinson, J., 1930, 423; Heilbron and Wilkinson, *ibid.*, p. 2537) the preparation of 2 : 3 : 5-trimethylnaphthalene is now described. *o*-Xylyl bromide was condensed with ethyl sodiomethylacetoacetate and the *ethyl o*-xylylmethylacetoacetate (I), obtained in good yield, was hydrolysed to β -*o*-tolyl-isopropyl methyl ketone (II), which was readily reduced to δ -*o*-tolyl- γ -methyl-sec.-butyl alcohol (III) by means of sodium and alcohol. The alcohol was converted through its bromide and cyanide into γ -*o*-tolyl- α -dimethylbutyric acid (IV), the yield of which was poor owing to the ready decomposition of the bromide. Elimination of hydrogen chloride from the corresponding butyryl chloride by the

use of aluminium chloride gave 1-*keto*-2:3:5-*trimethyl*-1:2:3:4-*tetrahydronaphthalene* (V), which was reduced by Clemmensen's method to 2:3:5-*trimethyl*-1:2:3:4-*tetrahydronaphthalene* (VI). On dehydrogenation of the latter with selenium in the usual manner 2:3:5-*trimethylnaphthalene* was obtained as a low-melting solid which was characterised by means of its *picrate* (m. p. 122°) and *styphnate* (m. p. 148—149°).



EXPERIMENTAL.

o-Xylyl bromide (80 g.) was added slowly to a well-cooled suspension of ethyl sodiomethylacetoacetate (from 64 g. of ester) in absolute alcohol (300 c.c.). The mixture was refluxed for 2 hours, the solvent removed, and the diluted product extracted with ether. The crude ester was fractionally distilled under reduced pressure, *ethyl o-xylylmethylacetoacetate* (I) being obtained as a colourless oil, b. p. 177—179°/20 mm. (Found: C, 72.2; H, 8.0. $C_{15}H_{20}O_3$ requires C, 72.6; H, 8.1%).

β -*o*-Tolylisopropyl Methyl Ketone (II).—Ethyl *o*-xylylmethylacetoacetate (47 g.) was refluxed for 16 hours with 10% sodium hydroxide solution (400 g.) and alcohol (40 c.c.), and the cold product extracted with ether. After removal of solvent from the dried ethereal solution, the oil was distilled in a vacuum, β -*o*-tolylisopropyl methyl ketone (II) being obtained as a sweet-smelling liquid (16 g.), b. p. 132—133°/20 mm. The *semicarbazone*, which was extremely rapidly formed, separated from alcohol in rectangular plates, m. p. 152—153° (Found: N, 18.2. $C_{13}H_{19}ON_2$ requires N, 18.0%).

δ -*o*-Tolyl- γ -methyl-*sec*-butyl Alcohol (III).—Sodium (20 g.) was added gradually to a well-stirred boiling solution of the above ketone (20 g.) in absolute alcohol (200 c.c.). The product was diluted with water, alcohol distilled off, and the residue extracted with ether. After removal of solvent from the extract, the product was distilled in a vacuum, the *sec*-butyl alcohol being obtained as a thick oil (15 g.), b. p. 152—153°/20 mm. (Found: C, 80.5; H, 10.2. $C_{12}H_{18}O$ requires C, 80.9; H, 10.1%).

γ-*o*-Tolyl- $\alpha\beta$ -dimethylbutyric Acid (IV).—The above alcohol (20 g.) was heated at 80° for 5 hours with a 30% solution of hydrogen bromide in glacial acetic acid (200 g.). The cold liquid was diluted with water and extracted with ether. The bromide was obtained as a heavy oil (17 g.) which distilled between 130—160°/25 mm. and contained unsaturated material, probably hydrocarbons formed by loss of hydrogen bromide. It was refluxed for 20 hours with a solution of potassium cyanide (15 g.) in aqueous alcohol, the nitrile extracted with ether and boiled for 15 hours with 10% amyl-alcoholic potassium hydroxide (5 g. KOH), the amyl alcohol removed with steam, and the residual solution acidified; *γ*-*o*-tolyl- $\alpha\beta$ -dimethylbutyric acid (IV) then separated as an oil (2 g.) which would not crystallise.

The acid chloride, prepared from the acid and thionyl chloride, was a mobile oil, b. p. 140—145°/15 mm. With dry ammonia in light petroleum it gave the *amide*, which crystallised from light petroleum-benzene in rosettes of needles, m. p. 73° [Found (micro) : C, 75.9; H, 9.0. C₁₃H₁₉ON requires C, 76.1; H, 9.3%].

1-*Keto*-2 : 3 : 5-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (V).—A solution of the acid chloride (1.5 g.) in petroleum (b. p. 80—90°) (5 c.c.) was added gradually to freshly prepared aluminium chloride (1.5 g.), suspended in the same solvent. When the initial vigorous reaction had ceased, the mixture was refluxed for 1 hour and then decomposed with ice-cold dilute hydrochloric acid. The *ketone* (V) was separated by ether extraction and obtained as an oil which rapidly solidified. It separated from light petroleum in needles (1 g.), m. p. 87° [Found (micro) : C, 83.2; H, 8.4. C₁₃H₁₆O requires C, 83.0; H, 8.5%].

2 : 3 : 5-*Trimethylnaphthalene*.—The ketone (1 g.) was reduced by boiling with concentrated hydrochloric acid (50 c.c.) and amalgamated zinc (10 g.) for 6 hours, and the crude tetrahydro-derivative (1 g.), which was isolated as an oil, was directly dehydrogenated by heating with selenium (1.5 g.) at 300° for 20 hours. The product was distilled over sodium in a vacuum and treated with warm alcoholic picric acid solution. 2 : 3 : 5-*Trimethylnaphthalene picrate* (0.4 g.) crystallised from alcohol in small reddish-brown needles, m. p. 122° [Found (micro) : N, 10.5. C₁₉H₁₇O₇N₃ requires N, 10.5%]. Decomposition of the picrate with dilute aqueous ammonia yielded the hydrocarbon as an oil which became solid at 0°, but owing to the small amount available could not be further purified. For further characterisation it was converted into the *styphnate*, which crystallised from alcohol in golden-yellow needles, m. p. 148—149° [Found (micro) : C, 54.8; H, 4.0; N, 10.4. C₁₉H₁₇O₈N₃ requires C, 54.9; H, 4.1; N, 10.1%].

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