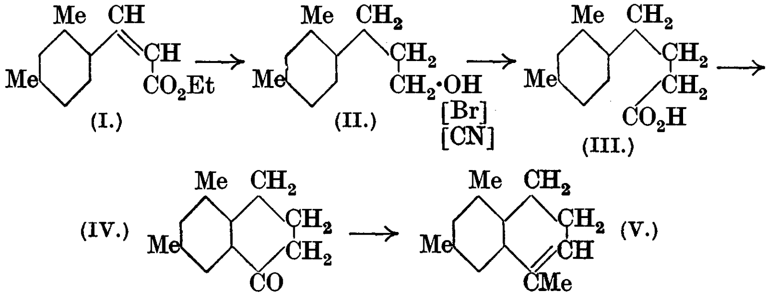
CCCXXXV.—*Synthesis of Alkyl Naphthalenes. Part II. 1 : 3 : 5- and 1 : 3 : 8-Trimethylnaphthalenes.*

By Isidor Morris Heilbron and Donald Graham Wilkinson.

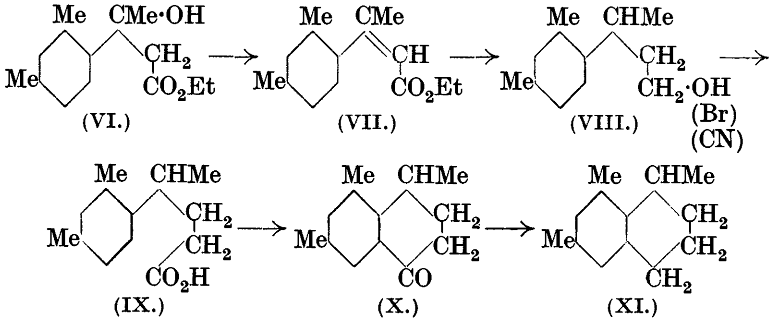
A description was given in Part I of this series (this vol., p. 423) of the synthesis of certain methylethylnaphthalenes. The work has now been extended to include trimethylnaphthalenes containing a methyl group in position 1 of the naphthalene nucleus. Of these, 1 : 2 : 6-trimethylnaphthalene has been described by Baeyer and Villiger (*Ber.*, 1899, **32**, 2447) and the 1 : 4 : 6-, 1 : 4 : 5-, 1 : 3 : 6-, and 1 : 3 : 7-isomerides have been prepared by Professor Ruzicka (private communication). The present paper deals with the synthesis of the 1 : 3 : 5- and 1 : 3 : 8-trimethylnaphthalenes.

1 : 3 : 5-*Trimethylnaphthalene.*—2 : 4-Dimethylbenzaldehyde was prepared as described by Gattermann (*Annalen*, 1906, **347**, 347) and converted into *ethyl* 2 : 4-*dimethylcinnamate* (I), which was reduced by Bouveault's method, a good yield of γ-(2 : 4-*dimethylphenyl*)-*propyl alcohol* (II) being obtained. This alcohol was converted, by way of the bromide and cyanide, into γ-(2 : 4-*dimethylphenyl*)-*butyric acid* (III), the chloride of which passed readily into 5-*keto*-1 : 3-*dimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (IV) on treatment with aluminium chloride. By the action of magnesium methyl iodide on the ketone an unstable carbinol was obtained which on treatment with acetic anhydride gave 1 : 3 : 5-*trimethyl*-7 : 8-*dihydronaphthalene* (V), from which 1 : 3 : 5-*trimethylnaphthalene* was obtained on treatment with selenium according to the method of Diels, Gädke, and Körding (*Annalen*, 1927, **459**, 1).



1 : 3 : 8-*Trimethylnaphthalene.*—The synthesis was commenced by condensing 2 : 4-dimethylacetophenone and ethyl bromoacetate in presence of zinc (compare Lindenbaum, *Ber.*, 1917, **50**, 1270), a mixture consisting of *ethyl* β-*hydroxy*-β-(2 : 4-*dimethylphenyl*)*butyrate* (VI) together with some *ethyl* β-(2 : 4-*dimethylphenyl*)*crotonate* (VII)

being obtained. This was completely converted without separation into the latter compound by treatment with phosphorus oxychloride in benzene (compare Lindenbaum, *loc. cit.*). Reduction of the unsaturated ester with sodium and alcohol gave γ-(2 : 4-*dimethylphenyl*)*butyl alcohol* (VIII), from which γ-(2 : 4-*dimethylphenyl*)-*valeric acid* (IX) was obtained in the usual manner. Elimination of hydrogen chloride from the *acid chloride* by means of aluminium chloride produced 5-*keto*-1 : 3 : 8-*trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (X). This ketone was reduced by Clemmensen's method to 1 : 3 : 8-*trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (XI), which was dehydrogenated by selenium to 1 : 3 : 8-*trimethylnaphthalene.*



EXPERIMENTAL.

Ethyl 2 : 4-*Dimethylcinnamate* (I).—2 : 4-Dimethylbenzaldehyde (43 g.) was added in small portions to dry ethyl acetate (200 c.c.) and fine sodium wire (7·4 g.) cooled to — 10°. The sodium rapidly dissolved and a brownish liquid was obtained, which, after standing over-night, was treated with glacial acetic acid (21 c.c.) and diluted with water. The ethyl acetate layer was separated, washed with sodium carbonate solution, and dried over sodium sulphate. After removal of solvent the residual oil was distilled; *ethyl* 2 : 4-*dimethylcinnamate*, b. p. 135—137°/5 mm., was then obtained as a highly refractive liquid (40 g.) (Found: C, 76·1; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%).

γ-(2 : 4-*Dimethylphenyl*)*propyl Alcohol* (II).—A solution of the ester (40 g.) in absolute alcohol (250 c.c.) was reduced with sodium (60 g.) by Rupe and Läuger's method (*Helv. Chim. Acta*, 1920, **3**, 272). The reduction furnished, together with the crude alcohol (19 g.), β-2 : 4-dimethylphenylpropionic acid (13 g.), from which a further quantity of alcohol was obtained by esterification and reduction. γ-(2 : 4-*Dimethylphenyl*)*propyl alcohol* was obtained on distillation under reduced pressure as a colourless viscous oil, b. p.

126°/5 mm. (Found : C, 80·0; H, 9·9. $C_{11}H_{16}O$ requires C, 80·5; H, 9·8%). The *urethane* crystallised from benzene–light petroleum in long fine needles, m. p. 81° (Found : N, 4·9. $C_{18}H_{21}O_2N$ requires N, 4·9%).

γ-(2 : 4-*Dimethylphenyl)propyl Bromide*.—The alcohol (20 g.) was heated under pressure with a 30% solution of hydrogen bromide in glacial acetic acid (200 g.) at 100° for 6 hours. When cool, the liquid was poured into water, and the bromide extracted with ether. The ethereal solution, freed from acid by shaking with sodium carbonate solution, was dried, and on evaporation furnished the bromide as a heavy oil (25 g.). γ-(2 : 4-*Dimethylphenyl)propyl bromide* formed a heavy mobile liquid, b. p. 147°/18 mm. (Found : Br, 35·6. $C_{11}H_{15}Br$ requires Br, 35·3%).

γ-(2 : 4-*Dimethylphenyl)butyric Acid* (III).—A solution of the bromide (25 g.) in alcohol (400 c.c.) was boiled with potassium cyanide (20 g. in 80 c.c. of water) for 24 hours. After removal of the alcohol the liquid was diluted with water and extracted with ether. The residual oil was distilled in a vacuum, the main portion passing over at 175—177°/23 mm. The residue, which solidified on cooling, consisted of the *amide* of the acid; it crystallised from benzene in fine silky needles, m. p. 128—129° (Found : N, 7·6. $C_{12}H_{17}ON$ requires N, 7·3%). The nitrile was hydrolysed with amyl-alcoholic potash; after removal of the amyl alcohol in steam the liquid was rendered acid and γ-(2 : 4-*dimethylphenyl)butyric acid* was precipitated (18 g.). The acid separated from light petroleum in lustrous plates, m. p. 78—79° (Found : C, 75·0; H, 8·4. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). The acid chloride formed a colourless liquid, b. p. 136—138°/9 mm.

5-*Keto*-1 : 3-*dimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (IV).—This was prepared from the acid chloride (17 g.) by treatment with aluminium chloride (15 g.) under similar conditions to those described in Part I (*loc. cit.*). It formed a colourless oil, b. p. 160°/14 mm. (13 g.). The *semicarbazone*, m. p. 243—246° (decomp.), crystallised from alcohol in minute needles (Found : C, 67·5; H, 7·7. $C_{13}H_{17}ON_3$ requires C, 67·5; H, 7·4%).

1 : 3 : 5-*Trimethyl*-7 : 8-*dihydronaphthalene* (V).—A solution of the above ketone (12·4 g.) in dry ether (50 c.c.) was added gradually from a tap funnel to a well-cooled solution of magnesium methyl iodide (from 40 g. of methyl iodide). The reaction was completed by refluxing for 2 hours, and the product decomposed with ice-cold dilute hydrochloric acid. The ether layer, which was separated and dried over sodium sulphate, yielded a viscous oil consisting mainly of the carbinol (10 g.). This was converted into 1 : 3 : 5-trimethyl-7 : 8-dihydronaphthalene by refluxing it with acetic

anhydride (50 c.c.) for 4 hours. The hydrocarbon was purified by distillation over sodium and obtained as a mobile liquid, b. p. 143—145°/18 mm. (7 g.).

1 : 3 : 5 - *Trimethylnaphthalene.*—The dihydro - derivative was dehydrogenated with selenium as described by Diels, Gädke, and Körding (*loc. cit.*). The crude product was converted into the *picrate*, which separated from alcohol in long orange needles, m. p. 141—142° (Found : C, 56·7; H, 4·5; N, 10·5. $C_{19}H_{17}O_7N_3$ requires C, 57·1; H, 4·3; N, 10·5%). On decomposition of the picrate with aqueous ammonia 1 : 3 : 5-*trimethylnaphthalene* was obtained; it crystallised from methyl alcohol in prisms, m. p. 47° (Found : C, 91·4; H, 8·2. $C_{13}H_{14}$ requires C, 91·8; H, 8·2%). The *styphnate* formed golden-yellow needles, m. p. 138° (Found : N, 9·9. $C_{19}H_{17}O_8N_3$ requires N, 10·1%).

Ethyl β-*Hydroxy*-β-(2 : 4-*dimethylphenyl*)*butyrate* (VI).—A mixture of 2 : 4-dimethylacetophenone (115 g.), prepared as described by Claus and Wöllner (*Ber.*, 1886, **19**, 230), and ethyl bromoacetate (130 g.) was added in small quantities at a time to pure zinc turnings (51 g.) covered with dry benzene in a flask fitted with a reflux condenser. After the addition of about 20 c.c. of the mixture the flask was heated on a steam-bath until the reaction commenced and finally the reaction mixture was refluxed for 1 hour. The product was decomposed with dilute sulphuric acid and extracted with ether. After removal of solvent the residual oil was distilled at 20 mm. pressure and separated into two main fractions, (a) b. p. 120—140°, (b) b. p. 170—180°. The lower-boiling fraction, which contained unchanged ketone together with ester, was treated with alkali, whereby β-*hydroxy*-β-(2 : 4-*dimethylphenyl*)*butyric acid* was obtained as an oil which solidified on standing. It crystallised from light petroleum–benzene in colourless needles, m. p. 70—72° (Found : C, 69·1; H, 8·1. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). The higher-boiling fraction (50 g.) consisted mainly of *ethyl -hydroxy*-β-(2 : 4-*dimethylphenyl*)*butyrate* (Found : C, 72·3; H, 8·7. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%).

Ethyl β-(2 : 4-*Dimethylphenyl*)*crotonate* (VII).—A solution of the hydroxy-ester (50 g.) in benzene (150 c.c.) was refluxed for 30 minutes with phosphorus oxychloride (10 c.c.). The cold solution was poured into water and the benzene layer was separated, washed with sodium carbonate solution, and dried over sodium sulphate. After removal of the benzene, the ester was distilled, the main fraction passing over at 160—170°/20 mm. (Found : C, 77·4; H, 8·5. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%).

γ-(2 : 4-*Dimethylphenyl*)*butyl Alcohol* (VIII).—The above ester (58 g.) was reduced with sodium (60 g.) and alcohol (300 c.c.) in the usual manner. The crude alcohol (20 g.) was distilled, the main portion (12 g.), b. p. 140—150°/15 mm., being collected. Pure γ-(2 : 4-*dimethylphenyl)butyl alcohol* formed a colourless viscous liquid, b. p. 152—153°/19 mm. (Found : C, 80·4; H, 10·2. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%).

In addition to the alcohol β-(2 : 4-*dimethylphenyl)butyric acid* was obtained in large amount. It crystallised from light petroleum in colourless prisms, m. p. 69° (Found : C, 75·1; H, 8·4. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). The *ethyl* ester was obtained as a colourless liquid, b. p. 168—170°/25 mm. (Found : C, 76·5; H, 8·9. $C_{14}H_{20}O_2$ requires C, 76·4; H, 9·1%). Further quantities of the alcohol were obtained from it in the following manner : A solution of the ester (28 g.) in propyl alcohol (170 c.c.) contained in the apparatus described by Rupe and Läuger (*loc. cit.*) was heated at 130°, and reduced by means of sodium (30 g.), added in small portions. When all the sodium had dissolved, water was added, and the propyl alcohol removed under reduced pressure. The yield of alcohol obtained in this way is more than 10% larger than that obtained by the use of ethyl alcohol.

The *bromide*, which was prepared in the usual manner, formed a heavy colourless liquid, b. p. 143°/17 mm. (Found: Br, 33·3. $C_{12}H_{17}Br$ requires Br, 33·2%).

γ-(2 : 4-*Dimethylphenyl)valeric acid* (IX) was prepared from the bromide through the nitrile as previously described. It was obtained as a viscous oil, b. p. 175°/9 mm. (Found: C, 75·2; H, 8·9. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%). The acid chloride, obtained from the acid by means of thionyl chloride, formed a pungent-smelling liquid, b. p. 157—160°/18 mm. The *amide* formed needles, m. p. 91—92°, from benzene–petroleum (Found : N, 7·0. $C_{13}H_{19}ON$ requires N, 6·8%).

5-*Keto*-1 : 3 : 8-*trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (X).—A solution of the acid chloride (29 g.) in petroleum, b. p. 90—100° (20 c.c.), was added gradually from a tap funnel to freshly prepared aluminium chloride (20 g.) covered with petroleum (20 c.c.) in a flask fitted with a reflux condenser. The reaction was completed by heating on a water-bath for 2 hours. The product was decomposed with ice-water and extracted with ether. After removal of solvent the ketone was distilled and obtained as a colourless oil, b. p. 174—176°/20 mm. (20 g.) (Found : C, 82·6; H, 8·7. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%). The *semicarbazone* melted at 220—222° (Found : N, 16·9. $C_{14}H_{19}ON_3$ requires N, 17·1%).

1 : 3 : 8-*Trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (XI).—The ketone (5 g.) was reduced by vigorous boiling with concentrated hydrochloric acid and amalgamated zinc (35 g.) for 10 hours. The

liquid was then steam-distilled, and the distillate extracted with ether. 1 : 3 : 8-Trimethyl-5 : 6 : 7 : 8-tetrahydronaphthalene (3 g.) was obtained as a colourless liquid, b. p. 133—136°/18·5 mm.

1 : 3 : 8-*Trimethylnaphthalene.*—The tetrahydro-derivative (5 g.) was heated with selenium (5 g.) at 300° for 20 hours. After purification by distillation over sodium in a vacuum the product was treated with an alcoholic solution of picric acid. The *picrate* separated from alcohol in small orange-red needles, m. p. 125° [Found : (micro) C, 57·2; H, 4·5; N, 10·3. $C_{19}H_{17}O_7N_3$ requires C, 57·1; H, 4·3; N, 10·5%].

1 : 3 : 8-*Trimethylnaphthalene* regenerated from the picrate crystallised from methyl alcohol in plates, m. p. 48° (liquefies when mixed with 1 : 3 : 5-trimethylnaphthalene, m. p. 47°) (Found : C, 91·7; H, 8·3. $C_{13}H_{14}$ requires C, 91·7; H, 8·3%).

The *styphnate* crystallised from alcohol in golden needles, m. p. 140·5° (Found : C, 55·1; H, 4·1. $C_{19}H_{17}O_8N_3$ requires C, 54·9; H, 4·1%).

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