# LVIII.—*Synthesis of Alkyl Naphthalenes. Part I. 5-, 6-, and 7-Ethyl-1-methylnaphthalenes.*

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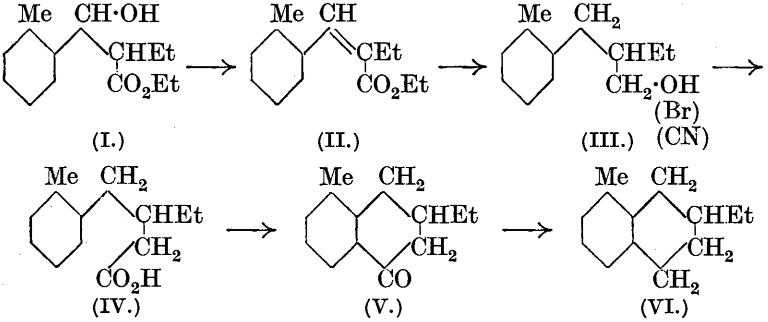
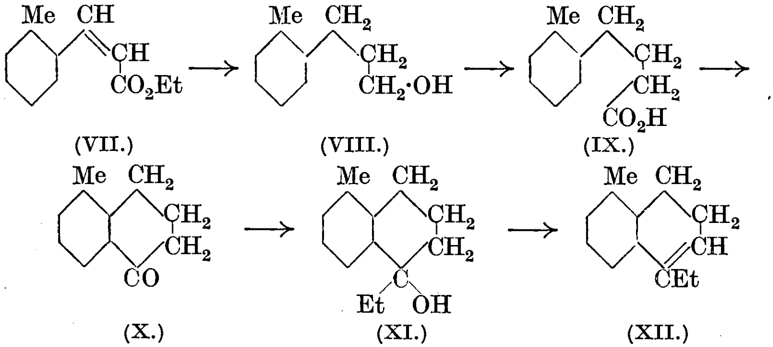
In connexion with the study now being carried out in this laboratory of the structure of the naphthalene hydrocarbon $C_{13}H_{14}$ obtained by dehydrogenation of tetra*cyclo*squalene with sulphur (Harvey, Heilbron, and Kamm, J., 1926, 3136) it became desirable to have, for reasons which will be explained in a later communication, information regarding the properties of the methylethylnaphthalenes containing a methyl group in position 1 and the ethyl radical in the second benzene ring. The present communication deals with the synthesis of the three isomerides indicated above.

1-*Methyl*-7-*ethylnaphthalene.*—*o*-Tolualdehyde and ethyl α-bromobutyrate were condensed together in presence of zinc, whereby *ethyl* β-*hydroxy*-β-o-*tolyl*-α-*ethylpropionate* (I) was obtained. The hydroxy-ester was converted into *ethyl* o-*methyl*-α-*ethylcinnamate* (II) by treatment with phosphorus tribromide and subsequent removal of hydrogen bromide by heating with diethylaniline. Reduction of the unsaturated ester by Bouveault's method gave the alcohol (III), which was converted through the *bromide* and nitrile (compare Ruzicka, *Helv. Chim. Acta*, 1922, **5**, 934) into γ-o-*tolyl*-β-*ethylbutyric acid* (IV). Ring closure was brought about by the action of aluminium chloride on the acid chloride of (IV), an almost theoretical yield of the cyclic *ketone* (V) being obtained. The ketone was reduced by Clemmensen's method to 1-*methyl*-7-*ethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (VI), and this on treatment with selenium (compare Diels, Gädke, and Körding, *Annalen*, 1927, **459**, 1) gave 1-*methyl*-7-*ethylnaphthalene.*



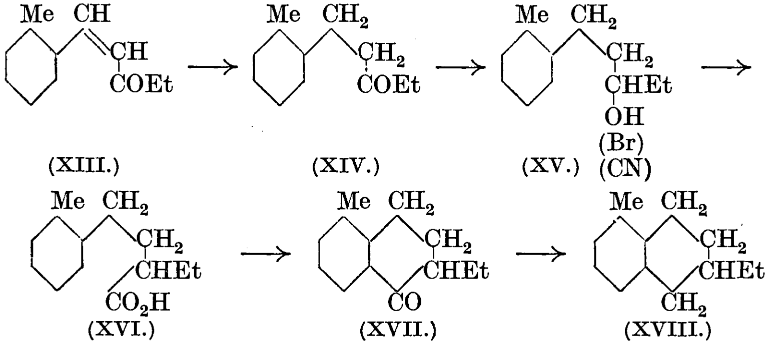
1-*Methyl*-5-*ethylnaphthalene.*—*o*-Tolualdehyde was condensed with ethyl acetate in presence of sodium, as described by Young (*Ber.*, 1892, **25**, 2102), to *ethyl* o-*methylcinnamate* (VII), which was reduced with sodium and alcohol, in the apparatus described by Rupe and Läuger (*Helv. Chim. Acta*, 1920, **3**, 272), to γ-*o*-tolylpropyl alcohol (VIII). The alcohol was converted through the *bromide* and the nitrile into γ-o-*tolylbutyric acid* (IX), from which 5-*keto*-1-*methyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (X) was obtained by the action of aluminium chloride on the acid chloride. The ketone on treatment with magnesium ethyl iodide yielded the hydroxy-compound (XI), which, on distillation or on heating with acetic anhydride, lost water, giving 1-*methyl*-5-*ethyl*-7 : 8-*dihydronaphthalene* (XII). Dehydrogenation of this hydrocarbon by means of selenium gave the required 1-methyl-5-ethylnaphthalene.



(VII.) (VIII.) (IX.)

(X.) (XI.) (XII.)

1-*Methyl*-6-*ethylnaphthalene*.—2-Methylstyryl ethyl ketone (XIII), prepared by the condensation of *o*-tolualdehyde with methyl ethyl ketone in presence of alkali, on hydrogenation in presence of colloidal palladium, gave β-o-*tolyldiethyl ketone* (XIV), and this on reduction with sodium gave a satisfactory yield of γ-o-*tolyl*-α-*ethylpropyl alcohol* (XV), from which γ-o-*tolyl*-α-*ethylbutyric acid* (XVI) was readily obtained in the usual manner. The acid was converted into its *acid chloride*, which on treatment with aluminium chloride gave an almost quantitative yield of 5-*keto*-1-*methyl*-6-*ethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (XVII). On reduction of the ketone by Clemmensen's method 1-*methyl*-6-*ethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (XVIII) was formed, and this was dehydrogenated with selenium, giving 1-*methyl*-6-*ethylnaphthalene*. A somewhat better yield of the alkylnaphthalene is obtained by reducing (XVII) with sodium and alcohol, whereby a mixture of carbinol and unsaturated hydrocarbon is produced which, without further purification, is treated with selenium.



(XIII.) (XIV.) (XV.)

(XVI.) (XVII.) (XVIII.)

## EXPERIMENTAL.

*Ethyl* β-*Hydroxy*-β-o-*tolyl*-α-*ethylpropionate* (I).—A mixture of ethyl α-bromobutyrate (72 g.) and freshly distilled *o*-tolualdehyde (45 g.) was added gradually to pure zinc turnings (26 g.) covered with dry benzene, in a flask fitted with a reflux condenser. After the addition of 20 c.c. of the mixture the flask was warmed on a steam-bath in order to start the reaction. The remainder was then added in small quantities at a time so as to regulate the reaction, and the whole refluxed for 4 hours. The product was decomposed with ice-cold dilute hydrochloric acid and the benzene layer was separated, washed with water, and dried over calcium chloride. After removal of the benzene the *hydroxy-ester* was fractionated in a vacuum and obtained as a thick oil (65 g.), b. p. 164—166°/12 mm. (Found : C, 70·8; H, 8·5. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%).

*Ethyl* o-*Methyl*-α-*ethylcinnamate* (II).—A solution of the hydroxy-ester (65 g.) in dry benzene (100 c.c.) was heated on a water-bath with phosphorus tribromide (85 g.) until the evolution of hydrogen bromide had practically ceased (5 hours). The excess of phosphorus tribromide was decomposed with alcohol (with ice-cooling), the solution poured into water, and the benzene layer separated and dried over calcium chloride. After removal of the solvent, the bromo-ester was obtained as a heavy oil (82 g.) with an irritating effect on the eyes. Without further purification, it was mixed with diethylaniline (70 g.) and heated at 180° for 4 hours. Water was added, the whole extracted with ether, and the excess of diethylaniline removed by repeated washing with dilute hydrochloric acid. The residual unsaturated ester was fractionated under reduced pressure, practically the whole distilling at 144°/15 mm.

γ-o-*Tolyl*-β-*ethylpropyl Alcohol* (III).—A solution of the above ester (45 g.) in absolute alcohol (300 c.c.) was placed in a flask fitted with a sealed stirrer, a reflux condenser, and a short wide inlet tube. The stirrer was set in rapid motion and sodium (65 g.), cut into small strips, was added gradually through the inlet tube to the boiling solution. During the course of the reduction (1½ hours) more alcohol (200 c.c.) was added from time to time to assist the solution of the sodium. The liquid was diluted with water, the alcohol distilled, and the residual alkaline solution extracted with ether. The ethereal solution, after being washed with water, dried, and evaporated, gave 19—20 g. of the crude alcohol. When the aqueous solution was rendered acid, β-o-*tolyl*-α-*ethylpropionic acid* was precipitated as an oil. After being extracted in ether, it distilled as a thick oil, b. p. 173—175°/12 mm., which gradually solidified, and then separated from light petroleum in large colourless prisms, m. p. 53—54° (Found : C, 75·0; H, 8·5. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). The acid was esterified and reduced as described above; a further quantity of γ-o-*tolyl*-β-*ethylpropyl alcohol* was then obtained. The whole was distilled, and the pure alcohol collected as a colourless viscous liquid, b. p. 145°/15 mm. (Found: C, 81·2; H, 10·2. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%).

γ-o-*Tolyl*-β-*ethylpropyl Bromide*.—The alcohol (25 g.) was heated under pressure with a 30% solution of hydrogen bromide in glacial acetic acid (250 g.) at 100° for 16 hours. The cooled liquid was poured into water; the bromide then separated as a heavy oil, which was extracted with ether. The ethereal solution was washed and dried, and the residual *bromide* distilled, b. p. 136—138°/12 mm. Yield, quantitative (Found: Br, 32·7. $C_{12}H_{17}Br$ requires Br, 33·2%).

γ-o-*Tolyl*-β-*ethylbutyric Acid* (IV).—A solution of the bromide (31 g.) in alcohol (500 c.c.) was boiled with potassium cyanide (25 g. in 70 c.c. of water) for 20 hours. The alcohol was then removed, and the residue diluted with water; the nitrile separated as an oil, which was directly hydrolysed by boiling for 40 hours with concentrated alcoholic potash (30 g. KOH). The crude acid was precipitated from the diluted alkaline solution, extracted with ether, and distilled, γ-o-*tolyl*-β-*ethylbutyric acid* being obtained as a thick oil (21 g.), b. p. 186°/13 mm. (Found: C, 75·4; H, 8·8. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%).

The acid chloride, prepared by treatment of the acid with thionyl chloride, was obtained as a colourless mobile oil, b. p. 149—150°/12 mm.

5-*Keto*-1-*methyl*-7-*ethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*.—A solution of γ-*o*-tolyl-β-ethylbutyryl chloride (19·5 g.) in petroleum (20 c.c., b. p. 80—100°) was gradually added to freshly prepared aluminium chloride (17 g.) covered with the same solvent. After the initial vigorous reaction had ceased, the mixture was heated on a steam-bath for 2 hours, and the product decomposed with ice-cold dilute hydrochloric acid. The ketone was extracted with ether and fractionated in a vacuum; a colourless oil, b. p. 165°/12 mm., was obtained which gradually solidified. On crystallisation from aqueous methyl alcohol, 5-*keto*-1-*methyl*-7-*ethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (17 g.) separated in small needles, m. p. 38° (Found: C, 82·7; H, 8·7. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%).

1-*Methyl*-7-*ethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*.—The ketone (15 g.) was reduced by boiling with concentrated hydrochloric acid and amalgamated zinc (100 g.). When the greater part of the zinc had dissolved, the liquid was steam-distilled and the distillate extracted with ether. The crude tetrahydronaphthalene was fractionated, giving a mobile oil (6 g.), b. p. 129—131°/14 mm.

1-*Methyl-7-ethylnaphthalene*.—The tetrahydro-derivative was heated with powdered selenium (6 g.) at 300° for 24 hours. The reaction product was distilled over sodium, yielding a colourless oil (4·8 g.), b. p. 134—138°/14 mm., which was directly treated with warm alcoholic picric acid solution. The crude *picrate* which separated on cooling was recrystallised from alcohol, giving long, silky, golden-yellow needles (5 g.), m. p. 97° (Found : C, 56·7 ; H, 4·3 ; N, 10·7. $C_{19}H_{17}O_7N_3$ requires C, 57·1 ; H, 4·3 ; N, 10·5%).

The picrate was decomposed with ammonia, and the hydrocarbon extracted with ether. 1-*Methyl*-7-*ethylnaphthalene* was obtained as a colourless oil, b. p. 133°/12 mm., $n_D^{20°}$ 1·5970, which failed to crystallise (Found : C, 91·4 ; H, 8·2. $C_{13}H_{14}$ requires C, 91·8 ; H, 8·2%).

*Ethyl* o-*methylcinnamate* (VII) was prepared as detailed by Young (*loc. cit.*) from *o*-tolualdehyde and ethyl acetate in presence of sodium. The pure ester, which does not appear to have been described, was obtained as a highly refractive liquid, b. p. 157°/25 mm. (Found : C, 75·8 ; H, 7·6. $C_{12}H_{14}O_2$ requires C, 75·8 ; H, 7·4%).

γ-*o*-Tolylpropyl alcohol (VIII), obtained by reduction of the above ester (25 g.) as described under γ-*o*-tolyl-β-ethylpropyl alcohol, formed a thick colourless oil (4 g.) with a sweetish odour, b. p. 136°/15 mm. The *urethane* formed long needles, m. p. 58°, from light petroleum (Found : N, 4·9. $C_{17}H_{19}O_2N$ requires N, 5·2%).

β-*o*-Tolylpropionic acid, which formed the main product (14 g.) in the Bouveault reduction, separated when the aqueous alkaline solution was rendered acid. It melted at 105° ; Young (*loc. cit.*) gives m. p. 102° (Found : C, 73·1 ; H, 7·4. Calc. for $C_{10}H_{12}O_2$ : C, 73·3 ; H, 7·3%). The acid was esterified, yielding 14 g. of the ethyl ester, b. p. 141°/22 mm., which was reduced to furnish a further quantity of the alcohol.

γ-o-*Tolylpropyl bromide* formed a heavy, sweet-smelling liquid, b. p. 124°/17 mm. Yield, quantitative (Found : Br, 37·7. $C_{10}H_{13}Br$ requires Br, 37·5%).

γ-o-*Tolylbutyric Acid* (IX).—A solution of the bromide (25·5 g.) in alcohol (450 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 the nitrile then separated as an oil. It was extracted with ether and hydrolysed with alcoholic potash (26 hours), and the diluted solution acidified ; γ-o-*tolylbutyric acid* was then precipitated as an oil which quickly solidified. On crystallisation from light petroleum it separated in needles (20 g.), m. p. 60° (Found : C, 74·3 ; H, 7·9. $C_{11}H_{14}O_2$ requires C, 74·2 ; H, 7·9%). The acid chloride was obtained as a colourless mobile liquid, b. p. 143°/17 mm.

5-*Keto*-1-*methyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (X) was prepared as described under (V). The reaction product was decomposed with ice-cold dilute hydrochloric acid, and the liquid steam-distilled. The distillate was extracted with ether; the ketone was then obtained as a crystalline solid. It separated from light petroleum in large crystals, m. p. 50—51° (yield, 5 g. from 7·5 g. of the acid chloride) (Found : C, 82·7; H, 7·7. $C_{11}H_{12}O$ requires C, 82·5; H, 7·5%).

1-*Methyl*-5-*ethyl*-7 : 8-*dihydronaphthalene* (XII).—A solution of the ketone (6 g.) in dry ether (25 c.c.) was added gradually to a well-cooled solution of magnesium ethyl iodide, prepared from magnesium (3·3 g.), ethyl iodide (20 g.), and dry ether (100 c.c.). The reaction mixture was heated under reflux for 4 hours and then decomposed with ice-cold dilute hydrochloric acid. The ethereal layer was washed with water and dried over sodium sulphate. After removal of the solvent the viscous carbinol was directly converted into the hydrocarbon by boiling with acetic anhydride (30 c.c.) under reflux for 1 hour. The acetic anhydride was decomposed with hot water and the hydrocarbon was extracted with ether and purified by distillation over sodium under reduced pressure; it was then obtained as a colourless mobile liquid (4·5 g.), b. p. 130—131°/12 mm.

1-*Methyl*-5-*ethylnaphthalene*.—The dihydro-compound (8 g.) was heated with selenium (4·2 g.) at 300° for 24 hours. The solid reaction product was distilled over sodium; the main portion, b. p. 133°/10 mm., was directly converted into picrate by treatment with warm alcoholic picric acid solution. On cooling, the *picrate* crystallised in small orange needles (13 g.), m. p. 97° (Found : C, 56·8; H, 4·4; N, 10·5. $C_{19}H_{17}O_7N_3$ requires C, 57·1; H, 4·4; N, 10·5%).

1-Methyl-5-ethylnaphthalene was regenerated by treating the picrate, suspended in ether, with dilute aqueous ammonia. It crystallised from alcohol in plates, m. p. 40°, closely resembling naphthalene in appearance and odour; $n_D^{30°}$ 1·600.

2-*Methylstyryl Ethyl Ketone* (XIII).—A solution of *o*-tolualdehyde (46 g.) and methyl ethyl ketone (52 g.) in 50% alcohol (800 c.c.) was treated with 2*N*-sodium hydroxide solution (20 c.c.), and the whole left over-night; 2-methylstyryl ethyl ketone then separated as a heavy yellow oil. After dilution with water the liquid was extracted with ether, and the ethereal solution dried over sodium sulphate. The residual oil was distilled, the main fraction passing over at 145—160°/14 mm. After further fractionation the ketone was obtained as a pale yellow oil (19 g.), b. p. 150—153°/14 mm.

The *semicarbazone*, prepared in the usual manner, crystallised from acetone in colourless needles, m. p. 176—178°; it exhibited phototropic properties, becoming bright yellow on exposure to sunlight (Found : N, 18·2. $C_{13}H_{17}ON_3$ requires N, 18·2%).

β-o-*Tolyldiethyl Ketone* (XIV).—2-Methylstyryl ethyl ketone (18 g.) was dissolved in dry ether (200 c.c.) and hydrogenated at room temperature in presence of palladium-black. After the absorption of hydrogen had ceased, the ether was removed and the residual oil distilled, the *ketone* being obtained as a pale yellow liquid (17 g.), b. p. 140—143°/16 mm. (Found : C, 81·4; H, 8·9. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%). The *semicarbazone* crystallised from alcohol in plates, m. p. 160° (Found : C, 66·6; H, 8·2; N, 18·2. $C_{13}H_{19}ON_3$ requires C, 66·9; H, 8·2; N, 18·0%).

γ-o-*Tolyl*-α-*ethylpropyl Alcohol* (XV).—A solution of the above ketone (15·2 g.) in boiling absolute alcohol (150 c.c.) was reduced by means of sodium (20 g.), added in small quantities at a time. The reaction mixture was diluted with water and extracted with ether. After removal of the solvent the alcohol was distilled in a vacuum, forming a colourless viscous oil (12·5 g.), b. p. 145—146°/14 mm. (Found : C, 80·7; H, 10·2. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%).

γ-o-*Tolyl*-α-*ethylpropyl bromide*, prepared as already described (p. 427), formed a colourless mobile liquid, b. p. 149—151°/18 mm. (Found : Br, 32·6. $C_{12}H_{17}Br$ requires Br, 33·2%).

γ-o-*Tolyl*-α-*ethylbutyric Acid* (XVI).—A solution of the bromide (12·5 g.) in alcohol (200 c.c.) was boiled with potassium cyanide (15 g. in 40 c.c. of water) for 30 hours. The alcohol was removed, and after dilution with water, the residue was extracted with ether. The crude product was distilled under reduced pressure, and yielded together with the nitrile fraction, b. p. 150—165°/16 mm. (6 g.), a lower-boiling fraction consisting of unsaturated hydrocarbons (3 g.). The nitrile was hydrolysed with amyl-alcoholic potash (potassium hydroxide, 10 g., in 100 c.c. of amyl alcohol) for 15 hours, and the amyl alcohol removed with steam. When the solution was acidified, γ-o-*tolyl*-α-*ethylbutyric acid* was precipitated as an oil, which was extracted with ether and distilled. The acid was collected as a viscous oil, b. p. 195—196°/18 mm., which solidified after some days. It crystallised from light petroleum in large prisms (4·5 g.), m. p. 51° (Found : C, 75·6; H, 8·8. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%). The acid chloride was obtained as a colourless liquid, b. p. 158—160°/18 mm.

5-*Keto*-1-*methyl*-6-*ethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (XVII) was prepared from the acid chloride (9 g.) as described on p. 427. The pure ketone (8 g.) was a colourless oil, b. p. 172°/19 mm. (Found : C, 82·9; H, 8·6. $C_{17}H_{16}O$ requires C, 83·0; H, 8·5%).

1-*Methyl*-6-*ethylnaphthalene*.—A portion of the ketone (3·7 g.)

was reduced by Clemmensen's method, giving 2 g. of 1-methyl-6-ethyl-5 : 6 : 7 : 8-tetrahydronaphthalene, b. p. 130°/16 mm. The remainder of the ketone (4·5 g.) was dissolved in alcohol and heated with sodium (7 g.) at 130°. After removal of the alcohol the liquid was diluted with water and extracted with ether. The residual oil was distilled, the greater part (2·4 g.) passing over at 110—160°/20 mm. It was unsaturated towards bromine, and was probably a mixture of unsaturated hydrocarbon and carbinol. The products from both experiments were mixed together and heated with an equal weight of selenium at 300° for 24 hours. The oil was diluted with ether, filtered from unchanged selenium, and purified by distillation over sodium. The crude hydrocarbon (3·1 g.), b. p. 145—152°/20 mm., was converted into the *picrate*, which crystallised from alcohol in small yellow needles, m. p. 82° (Found: C, 56·8; H, 4·4; N, 10·4. $C_{19}H_{17}O_7N_3$ requires C, 57·1; H, 4·3; N, 10·5%).

1-*Methyl*-6-*ethylnaphthalene*, which was regenerated from the pure picrate, formed a colourless, highly refractive liquid having a faint naphthalene-like odour; b. p. 140°/12 mm., $n_D^{20^\circ}$ 1·598 (Found: C, 91·4; H, 8·3. $C_{13}H_{14}$ requires C, 91·8; H, 8·2%).

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