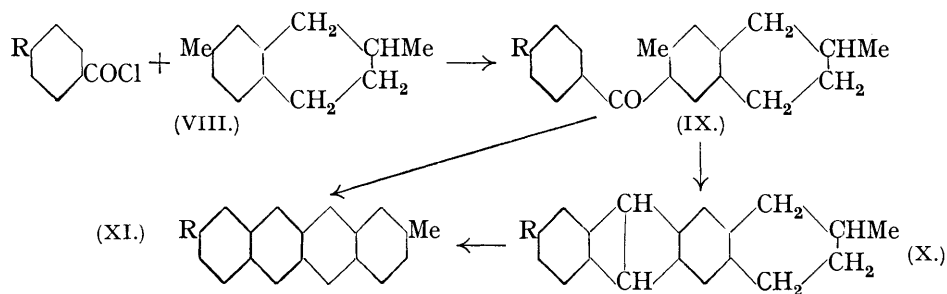


it slowly lost water and hydrogen, furnishing a mixture of three hydrocarbons: 2-methylnaphthacene (V), 6-methyl-1:2:3:4-tetrahydronaphthacene (VI), and 7-methyl-1:2-benzanthracene (VII). The first, a golden-orange substance of sparing solubility and high melting point, was easily separated from the mixture by fractional crystallisation. The residue containing the two last-mentioned compounds (which were less coloured but more fusible and soluble than the 2-methylnaphthacene) was dehydrogenated by heating with selenium, yielding a mixture readily separable into 2-methylnaphthacene and 7-methyl-1:2-benzanthracene.

(III) 2:6- and 2:7-Dimethyl-1:2:3:4-tetrahydronaphthalene: *Supplementary Syntheses of Naphthacene Homologues.*—By hydrogenation of 2:7-dimethylnaphthalene with a molybdenum catalyst prepared as described by Hall (*Fuel*, 1933, 12, 79) there may be obtained liquid products containing both 2:7-dimethyl-1:2:3:4-tetrahydronaphthalene (VIII) and 2:7-dimethyldecahydronaphthalenes. After heating for 4 hours at 300° with an initial pressure of 100 atmospheres of hydrogen, the product contained 2:7-dimethyl-1:2:3:4-tetrahydronaphthalene, b. p. 237°, and unchanged 2:7-dimethylnaphthalene, b. p. 265°; but when the temperature was raised to 390°, appreciable amounts of 2:7-dimethyldecahydronaphthalene, b. p. 216°, were formed and little or no 2:7-dimethylnaphthalene was unchanged.

Smooth and quantitative condensation of 2:7-dimethyl-1:2:3:4-tetrahydronaphthalene with benzoyl and *p*-toluoyl chlorides occurs under the influence of aluminium chloride, the products being 6-benzoyl- and 6-*p*-toluoyl-2:7-dimethyl-1:2:3:4-tetrahydronaphthalene (IX; R = H, CH₃). When these ketones are boiled, they yield as main products 2-methyl- and 2:7-dimethyl-1:2:3:4-tetrahydronaphthacene (X; R = H, CH₃), but there are also formed smaller amounts of 2-methyl- and 2:7-dimethyl-naphthacene (XI; R = H, CH₃).



In each case dehydrogenation of the tetrahydronaphthalene derivative is readily brought about by heating with selenium at 240°.

That the initial ketone has the indicated structure is shown by the ultimate production of a linear 4-ring hydrocarbon, but there is further evidence that the hydrogen atom in the 6-position in 2:7-dimethyl-1:2:3:4-tetrahydronaphthalene is, as would be expected, the most reactive. When treated with diphenylcarbonyl chloride, the hydrocarbon yields a dimethyltetrahydronaphthodiphenylamide, which when saponified gives the corresponding acid. The latter when dehydrogenated gives 3:6-dimethyl-2-naphthoic acid, identical with an authentic specimen, thus establishing the structure of the diphenylamide.

Sulphonation of 2:7-dimethyl-1:2:3:4-tetrahydronaphthalene in the cold gives a good yield of a homogeneous monosulphonic acid, of which the structure is shown by its conversion, on caustic potash fusion, into a mixture containing both the corresponding 2:7-dimethyl-1:2:3:4-tetrahydro-6-naphthol and 3:6-dimethyl-2-naphthol (compared with an authentic specimen).

Hydrogenation of 2:6-dimethylnaphthalene was effected by heating to 390° with hydrogen (initial pressure, 100 atmospheres) and the same catalyst as in the case of the 2:7-isomeride. The product contained both 2:6-dimethyl-1:2:3:4-tetrahydronaphthalene and 2:6-dimethyldecahydronaphthalene. At 300°, little or no hydrogenation took place,

from which it seems that 2 : 6-dimethylnaphthalene requires a higher temperature than the 2 : 7-isomeride before hydrogenation begins.

Condensation was effected between 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene and *p*-toluoyl chloride and the resulting 7-*p*-toluoyl-2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene pyrolysed to yield both 2 : 6-dimethylnaphthalene and 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene; the second was transformed into the first by heating with selenium. Experiments parallel to those with the 2 : 7-isomeride showed that in 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene the hydrogen atom in the 7-position was the most reactive. Two points of difference between the isomerides may be mentioned; derivatives of 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene are less readily dehydrogenated; and although both 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthol and 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydro-6-naphthol have "wetting-out" properties, the first-mentioned appears by a conventional test to be very much superior to the latter.

EXPERIMENTAL.

3 : 6-Dimethyl-2-naphthylamine.—3 : 6-Dimethyl-2-naphthol was prepared from 2 : 7-dimethylnaphthalene through 2 : 7-dimethylnaphthalene-3-sulphonic acid as described by Weissgerber and Kruber (*Ber.*, 1919, 52, 340). The naphthol (38 g.) was heated at 200° for 6 hours with 30 g. of ammonium sulphite and 400 c.c. of ammonia solution (*d* 0.880) in an autoclave, and the reaction product treated with excess of boiling dilute caustic soda solution, cooled, and extracted with ether. The crude hydrochloride of the base (30 g.; 65% of the theoretical yield) was precipitated when the ethereal extract was shaken with 10% hydrochloric acid. Unchanged naphthol (11.0 g.) was recovered from the aqueous alkaline solution. 3 : 6-Dimethyl-2-naphthylamine, obtained by digestion of the hydrochloride with warm dilute caustic soda, was readily soluble in alcohol or benzene; it crystallised from petroleum (b. p. 60—80°) in plates with satin-like sheen, m. p. 139° (Found : C, 84.2; H, 7.6. $C_{12}H_{13}N$ requires C, 84.2; H, 7.6%). The hydrochloride, colourless flakes, m. p. 283° (decomp.), is somewhat soluble in dilute hydrochloric acid (Found : Cl, 17.1. $C_{12}H_{13}N.HCl$ requires Cl, 17.1%). The acetyl derivative, m. p. 207°, separates from acetic acid or alcohol in tufts of colourless needles (Found : C, 78.9; H, 6.9. $C_{14}H_{15}ON$ requires C, 78.9; H, 7.0%).

3 : 6-Dimethyl-2-naphthonitrile.—The base (16.5 g.), suspended in 25 c.c. of concentrated dichloric acid and 80 c.c. of water, was diazotised at 0—5° with 8.0 g. of sodium nitrite, and the diazo-solution added to a cold Sandmeyer reagent, in a 4 l. flask, made from 34 g. of potassium cyanide, 30 g. of copper sulphate, and 160 c.c. of water. There was much effervescence when the first-formed precipitate was warmed to 100° and a suspension of the crude nitrile (11.0 g.) remained. Purified by sublimation and crystallisation from alcohol, 3 : 6-dimethyl-2-naphthonitrile formed tufts of colourless plates, m. p. 145° (Found : C, 86.0; H, 6.0. $C_{13}H_{11}N$ requires C, 86.2; H, 6.1%).

3 : 6-Dimethyl-2-naphthoic Acid.—The nitrile (from 16.5 g. of base) was heated with 50% caustic potash solution and alcohol for 24 hours. After dilution the solution was cooled and filtered, and the filtrate acidified, whereupon 3 : 6-dimethyl-2-naphthoic acid (11.0 g.) was precipitated. The acid crystallised from aqueous acetic acid in pale cream needles, m. p. 224°, sparingly soluble in water and soluble in acetic acid, alcohol, or benzene (Found : C, 77.9; H, 6.0. $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.0%).

3 : 6-Dimethyl-2-naphthoyl chloride, obtained in almost theoretical yield by refluxing the acid for 2 hours with 3 times its weight of thionyl chloride, was purified by fractional distillation in a vacuum, b. p. 160°/3 mm., and set on cooling in tufts of cream needles, m. p. 70° (Found : Cl, 15.9. $C_{13}H_{11}OCl$ requires Cl, 16.3%). The acid chloride reacts with aniline to give 3 : 6-dimethyl-2-naphthanilide, pale straw-coloured, lustrous flakes from alcohol, m. p. 207—208° (Found : C, 82.9; H, 6.4. $C_{19}H_{17}ON$ requires C, 82.9; H, 6.2%).

Preparation and Pyrolysis of 2-*p*-Toluoyl-3 : 6-dimethylnaphthalene : 2 : 7-Dimethylnaphthalene.—A small yield of the required ketone was obtained when 5.0 g. of 3 : 6-dimethyl-2-naphthoyl chloride, dissolved in dry toluene, were added, in portions, to 6.0 g. of sublimed ferric chloride covered with dry toluene, and the mixture heated at 90° for 4 hours. The product was decomposed with ice, and the toluene solution shaken with dilute caustic soda solution and water and evaporated to small bulk; 2-*p*-toluoyl-3 : 6-dimethylnaphthalene (0.5 g.) then slowly crystallised. The ketone separated from petroleum (b. p. 60—80°) in large colourless plates, m. p. 112° (Found : C, 87.3; H, 6.75. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%). When heated

at 400°, it readily charred but formed a small amount of an orange sublimate. This was recrystallised from acetic acid and yielded golden-orange plates of 2 : 7-dimethylnaphthacene, m. p. 362° (Found : * C, 93·6; H, 6·5. C₂₆H₁₆ requires C, 93·7; H, 6·3%). The hydrocarbon closely resembles its 2 : 6-isomeride; it is sparingly soluble in the common solvents and its solutions show marked green fluorescence. In cold concentrated sulphuric acid it dissolves to a moss-green solution. When mixed with 2 : 6-dimethylnaphthacene, there is no marked depression of m. p.

2 : 7-Dimethylnaphthacene-9 : 10-quinone.—To the hydrocarbon (1·0 g.), suspended in 50 c.c. of boiling acetic acid, were added 1·2 g. of potassium dichromate in portions. The quinone, precipitated on dilution with water, crystallised from acetic acid, in which it was fairly readily soluble, in minute, short, flattened, yellow needles, m. p. 233° (Found : C, 83·8; H, 5·2. C₂₀H₁₄O₂ requires C, 83·9; H, 4·9%). The deep purple-red colour of the solution in concentrated sulphuric acid fades on dilution.

6-(2' : 4'-Dimethyl)benzoyl-1 : 2 : 3 : 4-tetrahydronaphthalene (V).—Diphenylcarbonyl chloride (70 g.) was dissolved in tetralin (79 g.), an equal volume of carbon disulphide and powdered aluminium chloride (50 g.) were added, and the whole was heated under reflux for 3 hours. Carbon disulphide was then evaporated, and the residue poured on ice. The low-melting solid which separated, 1 : 2 : 3 : 4-tetrahydro-6-naphthodiphenylamide, crystallised from benzene-petroleum (b. p. 40—60°) in tufts of colourless, elongated, rhombic prisms, m. p. 87—88° (Found : C, 84·3; H, 6·7. C₂₃H₂₁ON requires C, 84·4; H, 6·4%). The crude amide was boiled for $\frac{1}{2}$ hour with 140 c.c. of concentrated sulphuric acid and 84 c.c. of water and, after dilution and cooling, the precipitated solid was dissolved in ether and shaken with dilute caustic soda solution. Acidification of the soda extract gave 52·5 g. of crude 1 : 2 : 3 : 4-tetrahydro-6-naphthoic acid, which was crystallised from benzene, yielding 34·5 g., m. p. 154°. The acid chloride was obtained quantitatively by heating the acid under reflux for 4 hours with 3 times its weight of thionyl chloride and fractionally distilling the product in a vacuum (b. p. 163°/12 mm.). The acid and its chloride have been prepared by less convenient methods by v. Braun, Kirschbaum, and Schuhmann (*Ber.*, 1920, 53, 1158, 1161). The acid chloride reacted with aniline to give 1 : 2 : 3 : 4-tetrahydro-6-naphthanilide, which crystallised from alcohol in colourless needles, m. p. 147° (Found : C, 80·9; H, 7·1. C₁₇H₁₇ON requires C, 81·25; H, 6·8%).

1 : 2 : 3 : 4-Tetrahydro-6-naphthoyl chloride (28 g.) was dissolved in an equal volume of carbon disulphide and added gradually to powdered aluminium chloride (30 g.) covered with *m*-xylene (30 g.). After heating under reflux for 3 hours, the carbon disulphide was evaporated, and the reaction product decomposed with water. The viscid ketone which separated was washed with dilute sodium carbonate solution and water, dried and fractionally distilled in a vacuum. Yield, 36·5 g. of b. p. 223°/10 mm. Similarly, from 30 g. of 2 : 4-dimethylbenzoyl chloride, 30 g. of tetralin, and 30 g. of aluminium chloride, there were obtained 35·5 g. of the same viscid ketone. 6-(2' : 4'-Dimethyl)benzoyl-1 : 2 : 3 : 4-tetrahydronaphthalene is a pale yellow, viscid liquid which does not set even on long keeping (Found : C, 86·6, 86·0; H, 7·6, 7·8. C₁₉H₂₀O requires C, 86·4; H, 7·6%).

Pyrolysis of 6-(2' : 4'-Dimethyl)benzoyl-1 : 2 : 3 : 4-tetrahydronaphthalene : 2-Methylnaphthacene.—When the ketone (50 g.) was boiled (bath temperature 400—420°), it darkened in colour and smoothly eliminated water. The product, cooled after 6 hours, partly crystallised. The crystals were separated, and the unchanged ketone repyrolysed. Finally about 30% conversion into a solid product, m. p. ca. 160°, was effected. The solid, fractionally crystallised from acetic acid, yielded 0·2 g. of 2-methylnaphthacene and a large fraction (15 g.) of a pale yellow, ill-defined, crystalline substance melting fairly sharply at 158° and consisting of 7-methyl-1 : 2 : 3 : 4-tetrahydronaphthacene (Calc. for C₁₉H₁₈ : C, 92·7; H, 7·3%) and 7-methyl-1 : 2-benzanthracene (Calc. for C₁₉H₁₄ : C, 94·2; H, 5·8%) (Found : C, 93·2, 93·5; H, 6·2, 6·2%). The mixture could not be separated by fractional crystallisation or by crystallisation of the mixed picrates and was dehydrogenated by heating with excess of selenium at 230° for 4 hours and then at 350° till nothing further sublimed. The sublimate (good yield) was fractionally crystallised from acetic acid and contained very pale yellow 7-methyl-1 : 2-benzanthracene, m. p. 181° (identified by oxidation to the corresponding quinone, m. p. 167°; Cook, J., 1932, 470), and 2-methylnaphthacene. The latter is a golden-orange hydrocarbon, m. p. 350°, similar in its properties to 2 : 6- and 2 : 7-dimethylnaphthacene but rather more soluble (Found : C, 93·2; H, 5·8. C₁₉H₁₄ requires C, 94·2; H, 5·8%). When oxidised with potassium dichromate in acetic acid, it gave a resinous substance (probably containing both 2-methylnaphthacene-9 : 10- and -11 : 12-quinones) which was not further examined.

Hydrogenation of 2 : 6- and 2 : 7-Dimethylnaphthalenes.—2 : 6-Dimethylnaphthalene was

first hydrogenated by C. C. Hall, who allowed full use to be made of his unpublished observations. The hydrocarbon (200 g.) was placed in a 2 l. autoclave with 100 atmospheres pressure of hydrogen and a catalyst made by impregnating 20 g. of active charcoal with a solution of 4 g. of molybdenum trioxide in ammonia solution, drying the mixture at 100°, and adding 4 g. of flowers of sulphur. The temperature was raised to 390—400° and maintained for 6 hours. On cooling, there was a residual pressure of 75 atmospheres; and the colourless liquid product, boiling between 180° and 244°, clearly contained more than one individual substance. Redistillation gave a fraction of b. p. 237—239° (25—30% of total product) which consisted of 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (Found : C, 90·3; H, 10·1. $C_{12}H_{16}$ requires C, 90·0; H, 10·0%). The limp colourless oil set on cooling and melted at 14—17°. A smaller fraction, b. p. 215—220°, was washed repeatedly with concentrated sulphuric acid, and water, dried, and distilled; it then boiled at 216—217° and had the composition of 2 : 6-dimethyldecalin. It was an oil which did not set when cooled to 0° and had a characteristic terpene-like odour (Found : C, 86·7; H, 13·4. $C_{12}H_{22}$ requires C, 86·8; H, 13·2%). Six racemic forms of stereoisomeric 2 : 6-dimethyldecalins are possible (3 derived from *cis*-decalin and 3 from the *trans*-isomeride) and if this fraction is a pure specimen of one of these it is probable that others are formed in the hydrogenation and are contained in the other fractions of b. p. below 237°. The latter were sulphonated together and gave a quantity of pure sodium 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-7-sulphonate when the crude salt was recrystallised from water.

When the hydrogenation was carried out at a lower temperature and for a shorter time, the product contained much unchanged 2 : 6-dimethylnaphthalene.

2 : 7-Dimethylnaphthalene (250 g.) was hydrogenated for 4 hours at 300° with an initial pressure of 100 atmospheres of hydrogen and the same proportion of the same catalyst. The crude water-white liquid hydrogenation product yielded, on fractional distillation, 70 g. of unchanged hydrocarbon; a liquid, boiling over the range 180—237°, which did not appear to contain a preponderant individual substance, but yielded an appreciable proportion of pure sodium 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-6-sulphonate; and 84 g. of 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 237—238°, m. p. below 0° (Found : C, 90·0; H, 10·1%). When the hydrogenation was effected at 390—400°, the product contained very little unchanged 2 : 7-dimethylnaphthalene and a smaller proportion of the tetralin, but an oil, of b. p. 216—218°, inert to concentrated sulphuric acid in the cold and of a fragrant terpene-like odour was separated by fractional distillation (Found : C, 86·6; H, 13·3%). If this is one of the 6 isomerides of 2 : 7-dimethyldecalin, others are probably contained in the rest of the hydrogenation product which boils between 180° and 235°.

2 : 6-Dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthoic Acid.—Powdered aluminium chloride (25 g.) was added to a mixture of diphenylcarbonyl chloride (35 g.), 2 : 6-dimethyltetralin (20 g.), and carbon disulphide (30 c.c.), and the whole warmed gently for 6 hours. Carbon disulphide was then evaporated, and the residue poured on ice. The crude viscid 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthodiphenylamide which separated was boiled during $\frac{1}{4}$ hour with 170 g. of 75% sulphuric acid and the mixture of crude acid and diphenylamine, which crystallised on cooling and dilution, was treated with cold dilute sodium carbonate solution. 2 : 6-Dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthoic acid (4·0 g.), precipitated from the soda solution, crystallised from aqueous acetic acid in colourless elongated prisms or needles, m. p. 183° (Found : C, 76·5; H, 8·1. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%). When heated with thrice its weight of selenium for 4 hours at 250—300°, it lost hydrogen, and the product, recrystallised from acetic acid, yielded 2 : 6-dimethyl-3-naphthoic acid, identified by comparison with an authentic specimen.

2 : 7-Dimethyl-1 : 2 : 3 : 4-tetrahydro-6-naphthoic Acid.—From 2 : 7-dimethyltetralin (22 g.) there was obtained, by similar methods to those described above, a poor yield (4·0 g.) of 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydro-6-naphthoic acid, colourless needles or prisms, m. p. 187° (Found : C, 76·5; H, 8·1%). On dehydrogenation (see 2 : 6-isomeride above) it yielded 3 : 6-dimethyl-2-naphthoic acid.

2 : 6-Dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthol.—When shaken at 40° with concentrated sulphuric acid (40 g.), 2 : 6-dimethyltetralin (20 g.) dissolved rapidly to a deep red solution. The crude sulphonic acid was precipitated on addition of water, but dissolved on further dilution. The barium salt was crystallised from water, in which it was slightly soluble, and converted into the sparingly soluble sodium sulphonate (25 g.). This was powdered, and heated on the steam-bath with an equal weight of phosphorus pentachloride for 1 hour, and the product treated with cold water to precipitate the viscid sulphonyl chloride, which was boiled with ammonia solution (d 0·880) for 3 hours. An almost theoretical yield (from the sodium sulphonate) of 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-7-sulphonamide, cream needles, m. p.

166—167°, from alcohol-water, resulted (Found : S, 13·3. $C_{12}H_{17}O_2NS$ requires S, 13·4%). The sodium salt (15 g.) was fused for $\frac{1}{4}$ hour at 300—340° with 60 g. of caustic potash and a few c.c. of water, and the product diluted and acidified. The dark brown, viscid precipitate was dissolved in ether, shaken with sodium bicarbonate solution and water, ether evaporated, and the residue distilled. The fraction, b. p. 280—300°, set on cooling and was crystallised from benzene-petroleum (b. p. 40—60°), 5 g. of 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthol, colourless needles of phenolic odour, m. p. 116°, being obtained (Found : C, 81·9; H, 9·0. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%). When it was mixed with four times its weight of a sample of phenols of low "wetting power," the "wetting time" fell from 240 to 26 seconds (see Morgan, Pratt, and Pettet, *J. Soc. Dyers and Colourists*, 1933, 49, 125). The tetrahydronaphthol was dehydrogenated by heating at 240° for 4 hours with selenium and gave 2 : 6-dimethyl-3-naphthol, identical with an authentic specimen.

2 : 7-Dimethyl-1 : 2 : 3 : 4-tetrahydro-6-naphthol.—2 : 7-Dimethyltetralin (20 g.) was sulphonated as readily as the 2 : 6-isomeride when shaken with concentrated sulphuric acid (40 g.). The product was diluted to 300 c.c., neutralised with caustic soda, boiled, and cooled, whereupon 25 g. of the sodium sulphonate crystallised in pearly flakes. 2 : 7-Dimethyl-1 : 2 : 3 : 4-tetrahydro-6-sulphonamide, cream needles, m. p. 145·5°, from aqueous alcohol, was obtained almost quantitatively through the sulphonyl chloride (see preparation of 2 : 6-isomeride, above) (Found : S, 13·4%). The sodium sulphonate (22 g.) was fused with caustic potash (90 g.) (see preparation of 2 : 6-isomeride, above) and gave 5 g. of a crude product, b. p. 260—300°, m. p. 90—130°, from which was isolated, by fractional distillation and crystallisation, 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydro-6-naphthol, colourless needles with phenolic odour, m. p. 87°, from benzene-petroleum (b. p. 40—60°) (Found : C, 81·95; H, 9·0. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%). The less volatile portion of the crude product was recrystallised from benzene-petroleum (b. p. 40—60°) and furnished flaky crystals of 3 : 6-dimethyl-2-naphthol, m. p. 172° (compared with an authentic specimen).

Condensation of 2 : 6- and 2 : 7-Dimethyltetralin with p-Toluoyl and Benzoyl Chlorides.—The dimethyltetralin was dissolved in an equal volume of carbon disulphide, the theoretical amount of acyl chloride added, and then an equal weight of powdered aluminium chloride in portions. After boiling during $\frac{1}{4}$ hour, the reaction product was poured on ice, the viscid ketone taken up in ether and shaken with dilute caustic soda solution and water, and, after removal of ether, the residual crude ketone purified by fractional distillation or crystallisation. In each case the yield was almost quantitative. 7-p-Toluoyl-2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene formed large colourless rhombs, m. p. 95°, from benzene-petroleum (b. p. 40—60°) (Found : C, 86·4; H, 8·1. $C_{20}H_{22}O$ requires C, 86·3; H, 7·9%).

6-Benzoyl-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene is a colourless viscid liquid, b. p. 202°/4 mm., 199°/3 mm. (Found : C, 86·1; H, 7·9. $C_{19}H_{20}O$ requires C, 86·4; H, 7·6%). 6-p-Toluoyl-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, a colourless viscid liquid, b. p. 199°/2 mm., crystallised when cooled to -80°, but melted on warming to room temperature (Found : C, 86·3; H, 8·1%).

Pyrolysis of Ketones.—When gently boiled under reflux, 7-p-toluoyl-2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene smoothly lost water, and to a less extent hydrogen. The pyrolytic product (yield, about 30%) was removed at intervals, and the recovered ketone repyrolysed. The solid product was fractionally crystallised from acetic acid and furnished a small quantity of the sparingly soluble 2 : 6-dimethylnaphthacene, m. p. 365°, but the rest consisted of 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthacene, pale yellow, anthracene-like flakes, m. p. 214° (Found : C, 92·4; H, 7·7. $C_{20}H_{20}$ requires C, 92·3; H, 7·7%). 6-Benzoyl-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene similarly yielded on pyrolysis 2-methylnaphthacene and 2-methyl-1 : 2 : 3 : 4-tetrahydronaphthacene, pale yellow flakes, m. p. 203° (Found : C, 92·7; H, 7·6. $C_{19}H_{18}$ requires C, 92·7; H, 7·3%). 6-Toluoyl-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene gave mainly 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthacene, pale yellow flakes from acetic acid, m. p. 210° (Found : C, 92·1; H, 7·5. $C_{20}H_{20}$ requires C, 92·3; H, 7·7%); but again a small amount of the dehydrogenated 2 : 7-dimethylnaphthacene was present in the crude product. The tetrahydro-derivatives are much more soluble than the naphthacene homologues and are easily separated from them.

Dehydrogenation of Tetrahydronaphthacene Derivatives.—2-Methyl-, 2 : 6- and 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthacenes were all dehydrogenated smoothly by heating with selenium at 240° for 4 hours. The temperature was raised to 300—350° and the corresponding naphthacene homologue, which sublimed, was recrystallised from acetic acid.

Oxidation of 2 : 6- and 2 : 7-Dimethyl-1 : 2 : 3 : 4-tetrahydronaphthacenes.—When the tetra-

hydro-derivatives (1 g.) were oxidised, by addition of potassium dichromate to a boiling acetic acid solution, mixed quinone-like products were obtained unless at least 2 g. of dichromate were used. From 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthacene there was then obtained a good yield of pure 2 : 7-dimethylnaphthacene-9 : 10-quinone, identified by analysis (Found : C, 83·6; H, 5·3%) and comparison by mixed m. p. with an authentic specimen. From the other isomeride there was similarly obtained 2 : 6-dimethylnaphthacene-9 : 10-quinone.

Thanks are due to Dr. J. J. Fox for the micro-analysis marked with an asterisk, to Mr. E. C. Holt for assistance in the preparative and analytical work, and to Professor Gilbert T. Morgan, O.B.E., F.R.S., Director of Chemical Research, for his interest and advice and for permission to publish these results.

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[Received, November 12th, 1934.]
