

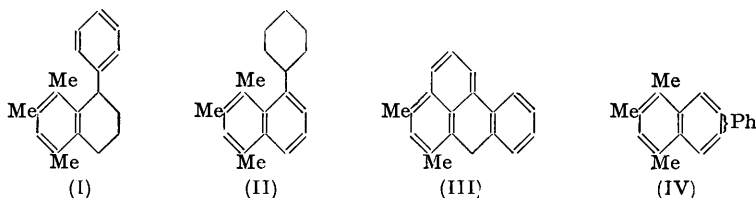
*The Elimination of Non-angular Alkyl Groups in Aromatisation  
Reactions. Part III.\**

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The dehydrogenation of the compounds (I) and (II) is described.

WHEN 1 : 2 : 3 : 4-tetrahydro-5 : 7 : 8-trimethyl-1-phenylnaphthalene (I) was dehydrogenated with selenium under conditions previously described\* it gave a mixture from which 2 : 4-dimethylmesobenzanthrene (III) was isolated. Light-absorption measurements however suggest that the mixture also contained 1 : 2 : 4-trimethyl-7(or 6)-phenylnaphthalene (IV). The latter compound and its 8-isomer (V) were obtained when (I) was dehydrogenated with palladised charcoal. No evidence was found to indicate that phenyl was lost in any of the reactions mentioned. By contrast, however, when 8-cyclohexyl-1 : 2 : 4-trimethylnaphthalene (II) was heated with selenium 1 : 2 : 4-trimethylnaphthalene was obtained.



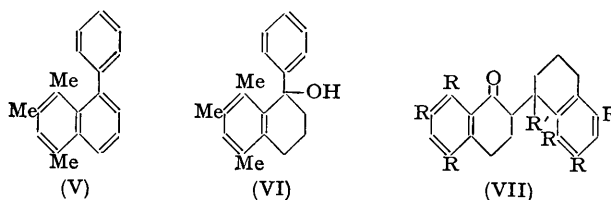
The trimethylphenylnaphthalenes were identified by comparison of their light-absorption spectra with those of 1- and 2-phenylnaphthalenes (cf. Friedel, Orchin, and Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199). There is close resemblance between the spectra of 2-phenylnaphthalene and (IV), but there is a somewhat greater difference between those of 1-phenylnaphthalene and (V). This is to be expected since there is appreciable hindrance to planarity in (V). In this connection it should be mentioned that neither of the compounds (IV and V) gave stable adducts with picric acid, styphnic acid, or trinitrobenzene, although each gave a highly coloured solution with these reagents. 1-Phenylnaphthalene similarly fails to give adducts; the more planar benzanthrene (III) readily gives a stable adduct with trinitrobenzene. 2-Phenylnaphthalene gives an adduct only with trinitrobenzene.

Spectral evidence does not distinguish between 1 : 2 : 4-trimethyl-6- and -7-phenylnaphthalene; (IV) may be either of these.

In an attempted preparation of (I), phenylmagnesium bromide was caused to react with 1 : 2 : 3 : 4-tetrahydro-5 : 7 : 8-trimethyl-1-oxonaphthalene (Cocker, Cross, and McCormick, *J.*, 1952, 72). The product was not the expected alcohol (VI) or its dehydration product. In fact the same product was obtained when cyclohexylmagnesium bromide was treated with the tetralone. Although the product fails to give any reactions of a ketone its light absorption is so similar to that of the ketone (VII; R = R' = H) (cf. Friedel and Orchin, "Ultra-Violet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, 1951, p. 136) that we feel justified in assigning the structure (VII; R = Me, R' = OH) to the new compound. Steric effects are no doubt responsible for the absence of ketonic properties (cf. Cagniant and Buu-Hoï, *Bull. Soc. chim.*, 1942, **9**, 841; Cocker *et al.*, *J.*, 1950, 1781). Vigorous reduction of this compound over Raney nickel in an autoclave gave 1 : 2 : 3 : 4-tetrahydro-5 : 7 : 8-trimethylnaphthalene. Cook and Lawrence (*J.*, 1936, 1431) obtained a compound presumed to be 1 : 2 : 3 : 4-tetrahydro-1-oxo-2-1'-tetralylidene-naphthalene (IX) from tetralone and cyclohexylmagnesium chloride. When (VII; R = Me, R' = OH) was heated alone at 150° or with acetic anhydride, the product was 1 : 2 : 3 : 4-tetrahydro-5 : 7 : 8-trimethyl-1-oxonaphthalene, produced no doubt by a reversed aldol

\* Parts I and II, *J.*, 1952, 72; 1953, 2355.

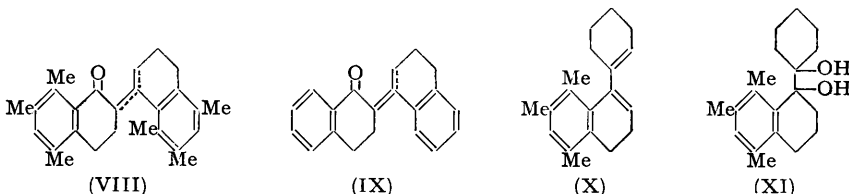
condensation. In contrast to the compound (IX) obtained by Cook and Lawrence (*loc. cit.*) neither of the two anhydro-compounds (VIII) can be set up in Courtauld models. It is not



surprising therefore that dehydration of (VII; R = Me, R' = OH) is impossible. Its reduction to 1 : 2 : 3 : 4-tetrahydro-5 : 7 : 8-trimethylnaphthalene probably proceeds *via* the tetralone. It is relevant that models show that the tetralylidene compound (IX) is much more strained than the corresponding dihydronaphthyl compound indicated in (IX) by the broken line.

Phenyl-lithium readily reacted with the trimethyltetralone to give the alcohol (VI); this was dehydrated with potassium hydrogen sulphate, and the product reduced, affording (I) in good yield.

8-cyclohexyl-1 : 2 : 4-trimethylnaphthalene could not be prepared by the method used for the phenyl analogue since it was found impossible to obtain *cyclohexyl-lithium* (cf. Gilman, Zoellner, and Selby, *J. Amer. Chem. Soc.*, 1933, 55, 1252). When however a mixture of 1 : 2 : 3 : 4-tetrahydro-5 : 7 : 8-trimethyl-1-oxonaphthalene and *cyclohexanone* was reduced with aluminium amalgam and the product dehydrated the dihydronaphthalene (X) was obtained. The mixed pinacol (XI) was presumably the intermediate, but this was not isolated. The formation of this pinacol agrees with Wieman's experience (*Compt. rend.*, 1941, 212, 1032) that it was the main product of the reduction of a mixture of *cyclohexanone* and ethyl methyl ketone. We were unable to reduce the compound (X): Cook and Lawrence (*loc. cit.*) found that 1-cyclohex-1'-enyl-naphthalene showed resistance to reduction. When however (X) was heated under pressure with hydrogen and Raney nickel, isomeric change occurred and a further hydrocarbon was produced, which presented a



single absorption maximum (2800 Å; log  $\epsilon$  3.90). Several structures could be assigned to this compound but in view of its properties (II) is the only reasonable one, and the light absorption can best be explained on steric grounds. Models show that (II) is under strain and lacks planarity.

#### EXPERIMENTAL

Light absorption measurements were made in EtOH.

1 : 2 : 3 : 4-Tetrahydro-1-hydroxy-5 : 7 : 8-trimethyl-1-phenylnaphthalene (VI).—Lithium (8 g.) was treated with bromobenzene (7.9 g.) in ether (100 c.c.), under nitrogen. 1 : 2 : 3 : 4-Tetrahydro-5 : 7 : 8-trimethyl-1-oxonaphthalene (6 g.) in ether (50 c.c.) was added, and the mixture was left overnight and then refluxed for 20 min. The product was decomposed with ice and hydrochloric acid, the ether solution was washed with sodium hydroxide, and the dried ethereal extract evaporated to yield the *alcohol* (9.4 g.), m. p. 83–84° (rhombs from ethyl acetate–light petroleum) (Found: C, 85.7; H, 8.2. C<sub>19</sub>H<sub>22</sub>O requires C, 85.7; H, 8.3%).

1 : 2-Dihydro-5 : 6 : 8-trimethyl-4-phenylnaphthalene.—The preceding compound (8.5 g.) was heated with freshly fused potassium hydrogen sulphate (20 g.) for 3 hr. at 155°, yielding the

*dihydro*-compound (4.7 g.), m. p. 89° (needles from alcohol) (Found : C, 91.5; H, 8.2.  $C_{19}H_{20}$  requires C, 91.9; H, 8.1%).

1 : 2 : 3 : 4-*Tetrahydro*-5 : 7 : 8-*trimethyl-1-phenylnaphthalene* (I).—The *dihydro*-compound (6 g.), reduced in ethyl acetate over Adams catalyst, gave the *tetrahydro*-compound (4.3 g.), m. p. 63° (needles from alcohol) (Found : C, 90.9; H, 9.0.  $C_{19}H_{22}$  requires C, 91.2; H, 8.8%).

*Dehydrogenation.* (a) The tetralin (1.5 g.) was heated for 4.5 hr. with palladised charcoal (1.5 g.) at 260—280°. The product was extracted with benzene and then treated with alcohol (15 c.c.), giving an insoluble fraction (A) (0.23 g.) and a solution from which a yellow solid (B) (0.3 g.) separated on cooling. The solid (B) crystallised from benzene–light petroleum as colourless needles, m. p. 133—134°, consisting of 1 : 2 : 4-*trimethyl-7(or 6)-phenylnaphthalene* (IV) (Found : C, 92.5; H, 7.3.  $C_{19}H_{18}$  requires C, 92.7; H, 7.3%). Light absorption : Max. at 2170, 2590, 2950 Å (log  $\epsilon$  4.51, 4.74, 3.91). Friedel, Orchin, and Reggel (*loc. cit.*) give 2120, 2500, 2850 Å (log  $\epsilon$  4.6, 4.7, 4.05) for 2-phenylnaphthalene.

Distillation of the mother-liquors from (IV) gave 1 : 2 : 4-*trimethyl-8-phenylnaphthalene* (V) (0.65 g.), b. p. 189—193°/4 mm., m. p. 77—78° (plates from light petroleum) (Found : C, 92.6; H, 7.2%). Light absorption : Max. at 2370, 3060 Å (log  $\epsilon$  4.65, 4.01). Friedel *et al.* (*loc. cit.*) give 2250, 2880 Å (log  $\epsilon$  4.75, 3.95) for 1-phenylnaphthalene.

Fraction (A) was chromatographed on alumina from benzene–light petroleum, yielding (V) (0.07 g.) and an unidentified solid (0.1 g.), m. p. 270°, which could not be crystallised but gave a brilliant green fluorescent solution in benzene.

(b) The tetralin (1.8 g.), dehydrogenated in the usual way with selenium, gave 2 : 4-*dimethyl-mesobenzanthrene* (III) (0.65 g.), b. p. 200—210°/4 mm., m. p. 82—83° (plates from alcohol) (Found : C, 91.6; H, 7.4.  $C_{19}H_{16}$  requires C, 93.4; H, 6.6%). Light absorption : Max. at 2340, 2500, 3350, 3530 Å (log  $\epsilon$  4.54, 4.25, 4.08, 4.03). Clar and Furneri (*Ber.*, 1932, 65, 1421) give 2280, 2500, 3120, 3290, 3440 Å (log  $\epsilon$  4.65, 4.20, 4.09, 4.24, 4.13) for benzanthrene. It is rapidly oxidised in air, hence the poor analyses. The *trinitrobenzene* adduct (scarlet needles from benzene–light petroleum) had m. p. 136° (Found : C, 66.0; H, 4.7.  $C_{25}H_{19}O_6N_3$  requires C, 65.6; H, 4.2%).

*Action of cycloHexyl- and Phenyl-magnesium bromide on 1 : 2 : 3 : 4-Tetrahydro-5 : 7 : 8-trimethyl-1-oxonaphthalene.*—The tetralone (6.3 g.) in ether (50 c.c.) was added to a solution from magnesium (0.83 g.) and cyclohexyl bromide (5.5 g.) or bromobenzene (5.2 g.) in ether (50 c.c.). The mixture was decomposed next morning in the usual way, yielding a solid (3.5 g.), m. p. 152—153° (prisms from chloroform–light petroleum) (Found : C, 82.3; H, 8.3.  $C_{26}H_{32}O_2$  requires C, 83.0; H, 8.5%). Light absorption : Max. at 2640 and 3160 Å (log  $\epsilon$  4.12, 3.39).

1 : 2 : 3 : 4-*Tetrahydro-5 : 7 : 8-trimethyl-1-naphthol.*—The corresponding tetralone (1.0 g.) was reduced in ether (110 c.c.) with lithium aluminium hydride (1 g.), yielding the *tetralol* (1 g.), m. p. 78° (needles from light petroleum–methyl alcohol) (Found : C, 81.9, H, 10.0.  $C_{15}H_{18}O$  requires C, 82.1; H, 9.5%).

1 : 2-*Dihydro-4-cyclohex-1'-enyl-5 : 7 : 8-trimethylnaphthalene* (X).—A mixture of the tetralone (9.4 g.), cyclohexanone (5 g.), and dry benzene (40 c.c.) was added to a mixture of aluminium foil (8 g.), dry benzene (100 c.c.), and anhydrous alcohol (200 c.c.), and the whole refluxed for 2 hr. Anhydrous alcohol (100 c.c.) was then added and the mixture was refluxed for a further 6 hr. The suspension was added to dilute hydrochloric acid, the organic layer separated, and the aqueous layer was extracted with benzene. From the combined organic extracts an oil was obtained which was refluxed for 2 hr. with acetic acid (50 c.c.) and acetic anhydride (50 c.c.). On cooling, the required *dihydronaphthalene* separated as needles (3.2 g.) and was further crystallised from acetic acid. It had m. p. 217° (rapid heating) (Found : C, 90.5; H, 8.8.  $C_{19}H_{24}$  requires C, 90.5; H, 9.5%). Light absorption : no maxima, the absorption falling in uniform manner from 2120 to 3100 Å with inflexion at 2600 Å. The low solubility in suitable solvents made quantitative measurement of absorption impossible. The compound gave a deep permanganate colour with concentrated sulphuric acid and rapidly decolorised permanganate.

8-cycloHexyl-1 : 2 : 4-*trimethylnaphthalene* (II).—The preceding compound (3 g.) in alcohol (150 g.) was heated in hydrogen with Raney nickel (1 g.) for 6 hr. at 150°/100 atm. The *naphthalene* crystallised from benzene–light petroleum as needles (2.4 g.), m. p. 158—159° (Found : C, 90.5; H, 9.3.  $C_{19}H_{24}$  requires C, 90.5; H, 9.5%). Light absorption : Max. at 2800 Å (log  $\epsilon$  3.90). It failed to give a picrate, but gave a scarlet colour with concentrated sulphuric acid. It decolorised permanganate only very slowly.

*Dehydrogenation.*—The naphthalene (1.4 g.), heated with selenium under the usual conditions, gave a product which on distillation gave two fractions, (A) (0.45 g.) b. p. 150—153°/14 mm., and (B) (0.4 g.) b. p. 180—210°/16 mm. The former crystallised from methyl alcohol as plates, m. p.

and mixed m. p. with authentic 1:2:4-trimethylnaphthalene 52—53°. Its picrate, m. p. 146—147°, was undepressed on admixture with that of 1:2:4-trimethylnaphthalene (cf. Ruzicka and Ehmann, *Helv. Chim. Acta*, 1932, 15, 140). Attempts to purify fraction (B) were unsuccessful. It did not give a picrate.

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