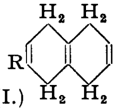
436. *Reduction by Dissolving Metals. Part IX.* Some Hydronaphthalene Derivatives.*

By A. J. Birch, (Miss) A. R. Murray, and Herchel Smith.

In connection with work on the synthesis of polycyclic hydroaromatic compounds related to the steroids some naphthalene and tetrahydronaphthalene derivatives have been reduced with sodium and alcohols in liquid ammonia to give a number of new tetra- and hexa-hydronaphthalene derivatives. Those carrying a methoxy- or 2-hydroxyethoxy-group attached to the dihydrobenzene ring have been hydrolysed by acids to hydronaphthyl ketones, of which (X) reacts by the Robinson–Mannich procedure to give a decahydroketophenanthrene.

Work in progress on polycyclic hydroaromatic compounds has made necessary an investigation of the partial reduction of benzenoid compounds containing more than one ring. The present communication reports some reductions of naphthalene and partly hydrogenated naphthalene derivatives by means of sodium and methanol or ethanol in liquid ammonia, with the principal object of preparing hydronaphthyl ketones as intermediates for further synthesis and as model compounds.

Naphthalene itself can be readily reduced to a crystalline tetrahydro-derivative which is probably 1 : 4 : 5 : 8-tetrahydronaphthalene (I; R = H). The double bonds are not conjugated because if this were so reduction would not stop at the tetrahydro-stage; furthermore, the substance possesses no light-absorption maximum in the region 2200—2800 A. 2-Methoxy- and 2-2′-hydroxyethoxy-naphthalene (II; R = OMe or $O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$) can similarly be reduced to what are probably the 1 : 4 : 5 : 8-tetrahydro-derivatives (I; R = OMe or $O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$). Careful hydrolysis of (I; R = $O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$) by dilute acid gave rise to the βγ-unsaturated ketone (III) which has no significant absorption in the region 2200—2800 A. and gives rise to an orange 2 : 4-dinitrophenylhydrazone converted by acid into the dark red derivative of (IV). The ketone (IV) could be obtained directly from (I; R = OMe) by more vigorous acid hydrolysis and possesses a maximum at 2800 A. which is indicative of two double bonds conjugated with the carbonyl group (Evans and Gillam, *J.*, 1945, 432). The action of a trace of toluene-*p*-sulphonic acid on (I; R = $O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$) produced a rise in temperature and formation of an isomeric substance, of lower boiling point and viscosity, which is formulated as the cyclic ketal (V) since it gave rise to the derivative of (III) by the action of Brady's reagent in the cold.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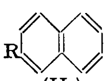
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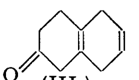
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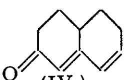
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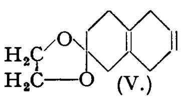
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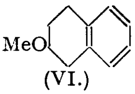
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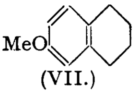
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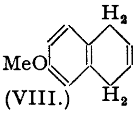
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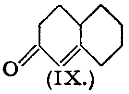
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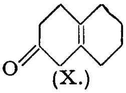
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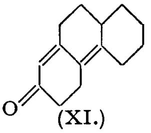
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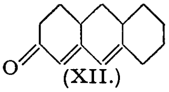
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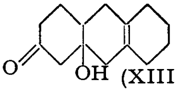
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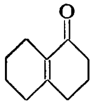
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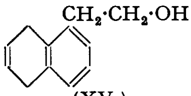
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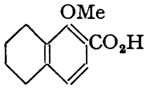
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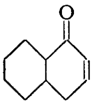
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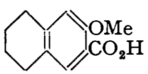
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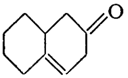
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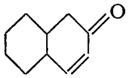
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* Part VIII, *J. Proc. Roy. Soc., N.S.W.*, 1950, **83**, 245.

αδ-Dihydrobenzene derivatives often disproportionate in the presence of hydrogenation catalysts (*e.g.*, γ-terpinene; Richter and Wolff, *Ber.*, 1930, **63**, 1721), and the action of Raney nickel on (I; R = OMe) was examined in the hope of obtaining a worthwhile yield of (VII). The reaction proceeded exothermally in ethanol, but the product contained about 15% of 2-methoxynaphthalene in addition to 25% of (VI) and 35% of (VII). The reaction is therefore of no practical importance for the preparation of the last substance, but is of interest in connection with the mechanism of the catalytic hydrogenation of naphthalenes, since it is evident that if compounds of the type (I) are intermediates in this process they will not long survive as such.

The preparation in good yield of 1 : 4-dihydro-6-methoxynaphthalene (VIII) would be of interest because 2-methoxynaphthalene normally is reduced in the substituted ring (Cornforth, Cornforth, and Robinson, *J.*, 1942, 689; Beer, D.Phil. Thesis, Oxford, 1948). An attempt was made to prepare it from (I; R = OMe) by partial oxidation with lead tetra-acetate (cf. Birch, *J.*, 1950, 1551). There seemed reason to expect that the methoxy-containing ring would be oxidised the more readily since an intermediate radical or cation formed by removal of H· or H^+ would probably be stabilised by an adjacent methoxyl group. With one mol. of lead tetra-acetate a 20% yield of (VIII) was proved by formation of the crystalline dibromide (cf. Beer, *loc. cit.*) accompanied by only a trace of the isomeric 2 : 5-dihydro-2-methoxynaphthalene. 2-Methoxynaphthalene was also formed. It seems probable that the use of a milder oxidising agent should give a better yield of (VIII), but interest in the process has diminished with the discovery that the B-ring of compounds of the equilenin type cannot be reduced by the metal–ammonia method (Birch and Smith, *J.*, 1951, 1882) and consequently the process would be useless for converting equilenin into equilin.

The reduction of 1 : 2 : 3 : 4-tetrahydro-6-methoxynaphthalene (VII) has already been briefly reported (Birch, *J.*, 1944, 430), the product identified after vigorous acid hydrolysis being (IX). Milder conditions have now been found to give (X), which, unlike (IX), gives rise to a bisulphite compound. The double bond shows a surprising stability in the βγ-position, and the Robinson–Mannich reaction gave rise to the phenanthrene ketone (XI) whose structure was proved by its absorption spectrum and dehydrogenation to phenanthrene. In an endeavour to increase the yield, the ketone (X) was condensed with ethyl formate before reaction with the Mannich base methiodide (Wilds, Shunk, and Hoffman, *J. Amer. Chem. Soc.*, 1949, **71**, 3266), but two other crystalline compounds resulted which are formulated as (XII) and (XIII) respectively, the latter being converted into the former by the action of alkali. The absorption spectrum of the 2 : 4-dinitrophenylhydrazone of (XII) confirms the presence of two double bonds conjugated with the carbonyl group. The infra-red absorption spectrum of (XIII) shows the carbonyl band at 5·82 μ., and a hydroxyl band at 2·97 μ.; there is no indication of a double bond in the 6-μ. region, and consequently this bond must be situated as shown. Compound (XII) was dehydrogenated to anthracene.

The reduction of 1 : 2 : 3 : 4-tetrahydro-5-methoxynaphthalene, followed by acid hydrolysis, has been shown to produce 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-1-ketonaphthalene (XIV) (Birch, *loc. cit.*), but the product was not easy to purify. The use of aryl 2-hydroxyethyl ethers (Birch and Mukherji, *J.*, 1949, 2531) facilitates reduction by increasing solubility, and also facilitates purification. 1 : 2 : 3 : 4-Tetrahydro-5-2′-hydroxyethoxynaphthalene was reduced more readily than the methoxy-analogue, although still with some difficulty, and after acid hydrolysis (XIV) was isolated, mixed with a little decahydro-1-ketonaphthalene. 1-2′-Hydroxyethoxynaphthalene was readily reduced to the crystalline dihydro-derivative (XV), but further reduction was difficult and yielded a mixture of hydrocarbons containing some (I; R = H), together with material which on acid hydrolysis formed a mixture of ketones.

Double bonds in positions different from those found in the products of direct reduction would result if reduction could be forced to occur in positions carrying a saturated carbon atom. In order to do this an electron-attracting group must be present which has a more powerful orientating influence than that of the electron-repelling saturated substituent; a group which is, moreover, readily removed if necessary. The most obvious one is carboxyl, which, if *ortho* to the alkoxy-group, can be eliminated by decarboxylation after acid hydrolysis to a β-keto-acid. The Kolbe reaction on 1 : 2 : 3 : 4-tetrahydro-5- and -6-hydroxynaphthalene, followed by methylation with a very large excess of methyl sulphate produced the acids (XVI) and (XVIII) which were reduced with sodium and ethanol in ammonia. From (XVI) was obtained, after acid hydrolysis and removal of the acidic fraction, a poor yield of a crystalline ketone (XVII), and from (XVIII) a poor yield of a mixture of ketones probably (XIX) and (XX). In both cases the preponderant product was acidic, and was not closely examined. That from

(XVI) was found to produce by the action of chromic acid a high yield of 1 : 2 : 3 : 4-tetrahydro-6-naphthoic acid, and probably consists essentially of 2 : 5 : 6 : 7 : 8 : 10-hexahydro-2-naphthoic acid produced by removal of methoxyl and reduction of the ring. This process is known to occur to a large extent with *o*- and *p*-anisic acid. The yields of ketone were too small for practical application, although compounds not accessible by other means were produced. The reduction of some other polycyclic systems is being examined.

EXPERIMENTAL.

1 : 4 : 5 : 8-*Tetrahydronaphthalene* (I; R = H).—Naphthalene (10 g.) in ethanol (40 c.c.) and ether (50 c.c.) was added rapidly to liquid ammonia (250 c.c.), with rapid stirring to give a fine precipitate. Sodium (15 g.) was added in small pieces, the reacion being at first very vigorous. Water (200 c.c.) was then added, and the solid removed by filtration, well washed with water, dried, and crystallised from methanol. 1 : 4 : 5 : 8-*Tetrahydronaphthalene* so obtained formed large plates (6·2 g.), m. p. 42° (Found : C, 87·1; H, 12·6. C_8H_{14} requires C, 87·3; H, 12·7%). It resembled naphthalene in appearance, but the odour was fainter and more pleasant; it failed to give adducts with picric acid or trinitrobenzene, and rapidly became brown and sticky in air.

1 : 4 : 5 : 8-*Tetrahydro-2-methoxynaphthalene* (I; R = OMe).—2-Methoxynaphthalene (7 g.) in warm ethanol (25 c.c.) was stirred into ammonia (300 c.c.) and reduced with sodium (7 g.). After working up in the usual manner, distillation gave 1 : 4 : 5 : 8-*tetrahydro-2-methoxynaphthalene* as an oil, b. p. 128°/10 mm., 136—137°/17 mm. (5·8 g.) (Found : C, 81·0; H, 8·8. $C_{11}H_{14}O$ requires C, 81·4; H, 8·6%). Hydrolysis by refluxing sulphuric acid (5%) for 2 hours, and distillation gave 2 : 3 : 4 : 5 : 6 : 10-*hexahydro-2-ketonaphthalene*, b. p. 137—140°/12 mm. (4·4 g.), $\lambda_{max.}$ 2800 A. (ε 14,800) (Found : C, 80·9; H, 8·4. $C_{10}H_{12}O$ requires C, 81·0; H, 8·1%). It gave a derivative with Brady's reagent as purple-red needles (from ethyl acetate), m. p. 202°, and a *semicarbazone* as cream-coloured prisms (from ethanol), m. p. 210—212° (Found : C, 64·0; H, 7·3. $C_{11}H_{15}ON_3$ requires C, 64·4; H, 7·3%).

1 : 4 : 5 : 8-*Tetrahydro*-2-2′-*hydroxyethoxynaphthalene*.—2-2′-Hydroxyethoxynaphthalene was prepared in the standard manner from β-naphthol and ethylene chlorohydrin in hot aqueous sodium hydroxide and had m. p. 63°, although Harnack (*J. Amer. Chem. Soc.*, 1920, **42**, 164) gives m. p. 76—77°. The naphthalene derivative (19 g.) in methanol (60 c.c.) was added to ammonia (500 c.c.), followed by sodium (21 g.) during 30 minutes with stirring. When reaction was complete, water (200 c.c.) was added, and the product extracted with ether and distilled, to give 1 : 4 : 5 : 8-*tetrahydro*-2-2′-*hydroxyethoxynaphthalene* (12 g.), b. p. 156—157°/1 mm., m. p. 65° (Found : C, 74·6; H, 8·5. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). This ether (2 g.) was shaken with a saturated solution of sodium hydrogen sulphite for 3 hours, the solid adduct decomposed with sodium carbonate, and the small amount of oil distilled; 1 : 2 : 3 : 4 : 5 : 8-*hexahydro-2-ketonaphthalene* had b. p. 85—90°/0·3 mm. (Found : C, 81·0; H, 7·8. $C_{10}H_{12}O$ requires C, 81·0; H, 8·1%). The only band in the ultra-violet above 2200 A. was a small one at $\lambda_{max.}$ 2740 (ε 200) (ethanol), probably due in part to the carbonyl group and in part to impurity. The 2 : 4-dinitrophenylhydrazone had m. p. 171°. After addition of a small crystal of toluene-*p*-sulphonic acid to the tetrahydrohydroxyethoxynaphthalene (1·1 g.) the temperature immediately rose. After 10 minutes the mixture was neutralised with gaseous ammonia and distilled, having b. p. 108—109°/0·8 mm. The substance appears to be 1 : 2 : 3 : 4 : 5 : 8-*hexahydro-2-ketonaphthalene ethylene ketal* (1 : 2 : 3 : 4 : 5 : 8 : 4′ : 5′-*octahydro*-1′ : 2′-*dioxole*-2′-spiro-2-*naphthalene*) (V) (Found : C, 74·7; H, 7·9. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%).

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*Octahydro-2-ketonaphthalene* (X).—1 : 2 : 3 : 4-Tetrahydro-6-methoxynaphthalene (40 g.; Stork, *J. Amer. Chem. Soc.*, 1947, **69**, 576) in ethanol (400 c.c.), ether (400 c.c.), and ammonia (2·5 l.) was reduced with sodium (40 g.). The product, worked up as usual, was dissolved in a little ether and shaken for 1·5 hours with hydrochloric acid at pH 2—3, and the resulting oil shaken with aqueous sodium hydrogen sulphite for 4 hours. The solid adduct was separated by centrifugation followed by filtration, and thoroughly washed with ether. The ethereal filtrate was concentrated and re-treated with sodium hydrogen sulphite. Four such treatments resulted in the separation of 36 g. of adduct. For some reason as yet undefined one treatment, no matter how prolonged, was insufficient. The solid was decomposed by shaking it with N-sodium carbonate solution (500 c.c.) and ether (300 c.c.), followed by further ether-extraction. 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*Octahydro-2-ketonaphthalene* so obtained (12 g.) had b. p. 85—87°/1·25 mm. (Found : C, 79·8; H, 9·1. $C_{10}H_{14}O$ requires C, 80·0; H, 9·35%). The ultra-violet absorption showed a small band at $\lambda_{max.}$ 2810 A. (ε 37·9), $\lambda_{min.}$ 2700 A. (ε 35·5). The 2 : 4-*dinitrophenylhydrazone* was obtained as yellow needles (from ethyl acetate–ethanol), m. p. 167·5—168·5° (Found : C, 58·5; H, 5·7; N, 17·15. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·45; N, 17·0%).

The residual material after the bisulphite treatment gave a fraction, b. p. 44—70°/1 mm., which did not react with Brady's reagent, and a fraction (5·1 g.), b. p. 79—83°/1 mm., which gave rise to the 2 : 4-dinitrophenylhydrazone, m. p. 169—171°, of the isomeric conjugated ketone 1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-octahydro-6-ketonaphthalene. Attempts to alkylate 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-2-ketonaphthalene with 2-phenylethyl bromide and sodium or potassium amide in liquid ammonia, benzene, or ether, resulted surprisingly in recovery of most of the ketone.

2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 14-*Decahydro-2-ketophenanthrene* (XI).—Diethylaminobutanone (4·315 g.) (Wilds and Shunk, *J. Amer. Chem. Soc.*, 1943, **65**, 469) was treated with methyl iodide (4·29 g.) in a 500-c.c. flask, the technique of Cornforth and Robinson (*J.*, 1949, 1855) being used. To it was added 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-2-ketonaphthalene (4·526 g.) in benzene (20 c.c.), under a nitrogen atmosphere, followed by a solution of potassium (1·175 g.) in ethanol (20 c.c.) during 5 minutes with ice-cooling. The flask was swirled until the methiodide had disappeared, the mixture left for 1 hour, refluxed for 5 minutes, cooled, and acidified with 2N-sulphuric acid, and the product extracted with ether.

The dark red oil so obtained was dissolved in light petroleum (b. p. 60—80°) and passed through a column of activated alumina, elution being carried out with light petroleum (b. p. 60—80°). The fraction so obtained (0·82 g.) consisted essentially of unchanged octalone, and the addition of increasing amounts of ethyl acetate, up to 10%, to the eluent then gave first a mixture (0·91 g.) forming a non-crystalline derivative with Brady's reagent, followed by a viscous oil (0·8 g.) giving rise to 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 14-*decahydro-2-ketophenanthrene* 2 : 4-*dinitrophenylhydrazone* as cherry-red needles (from ethyl acetate–ethanol), m. p. 175° (Found : C, 62·7; H, 5·6; N, 14·6. $C_{20}H_{22}O_4N_4$ requires C, 62·8; H, 5·8; N, 14·7%). The absorption at $\lambda_{max.}$ 4000 (ε 20,000), $\lambda_{max.}$ 2595 A. (ε 16,700) (in chloroform) indicates the presence of conjugated double bonds in the ketone (cf. Braude and Jones, *loc. cit.*; Djerassi and Ryan, *J. Amer. Chem. Soc.*, 1949, **71**, 1000). The remaining material on the column was a yellow-brown fluorescent gum, not showing phenolic properties and giving an amorphous derivative with Brady's reagent.

The crude decahydroketophenanthrene (0·8 g.) was reduced with sodium (5 g.) and ethanol (50 c.c.), and then dehydrogenated with 25% palladium–charcoal (105 mg.) at 290—300° for 3 hours. The product was extracted with benzene and passed through an alumina column to remove gross impurities. The semi-solid product was then chromatographed in light petroleum (b. p. 40—60°), the first gummy eluate being followed by phenanthrene (210 mg.), m. p. 98—98·5° (picrate, m. p. 143—144°; trinitrobenzene complex, m. p. 162°); all these m. p.s were undepressed by authentic specimens.

2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11 : 14-*Decahydro-2-ketoanthracene* (XII).—Ethyl formate (15 c.c.) in benzene (15 c.c.) was added under nitrogen to pure dry sodium methoxide from the metal (2·154 g.) and, after 15 minutes, 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-2-ketonaphthalene (4·4 g.) was added in benzene (25 c.c.). The deep yellow mixture was left for 1·5 hours and worked up as usual for the isolation of the formyl compound, a brownish oil, which, after being kept at 0·1 mm. for 3 hours (nitrogen), solidified to a buff-coloured solid (4·9 g.) giving an intense purple colour with alcoholic ferric chloride. It was treated with diethylaminobutanone (3·94 g.), methyl iodide (3·92 g.), and potassium (1·205 g.) in ethanol (30 c.c.) as described above, and the reaction product refluxed for 25 minutes under nitrogen after the addition of a further amount (0·41 g.) of potassium in ethanol (30 c.c.). After acidification with 2N-sulphuric acid the mixture was thoroughly extracted with ether, the ethereal solution washed with 2% sodium hydroxide solution to remove unchanged formyl compound (1·36 g.), and the ether was removed. The viscous oil was taken up in light petroleum (b. p. 40—60°) containing a few drops of ethyl acetate, whereupon a solid was precipitated as colourless needles, m. p. 178—184° after crystallisation from benzene. Good analyses were difficult to obtain, apparently because of retention of solvent, but after sublimation at 100°/6 × 10^{-4} mm. analyses were approximately correct for 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-*dodecahydro*-13-*hydroxy*-2-*ketoanthracene* (Found : C, 75·9; H, 9.2. $C_{14}H_{20}O_2$ requires C, 76·4; H, 9·0%). The m. p. range, unchanged by crystallisation, may be indicative of admixture of a stereoisomer, or of decomposition.

The viscous oil obtained by evaporation of the mother-liquor from the above crystallisation was dissolved in methanol (50 c.c.) and added to potassium hydroxide (20 g.) in methanol (450 c.c.) and water (40 c.c.) under nitrogen. After 2·5 hours the solution was poured into brine (1500 c.c.) and extracted with ether (4 × 200 c.c.). The brown oil on distillation gave a fraction (1·53 g.), b. p. 155—160°/0·1 mm., which solidified. This was taken up in light petroleum (b. p. 60—80°) and chromatographed on alumina (30 g.), with light petroleum (b. p. 60—80°) as the eluent. The first material obtained was a little non-ketonic oil, followed by crystalline material (0·600 g.). The 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11 : 14-*decahydro-2-ketoanthracene* crystallised from light petroleum (b. p. 40—60°) as needles, m. p. 102—103° (Found : C, 83·4; H, 9·2. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%). The absorption (ethanol) showed a band at $\lambda_{max.}$ 2940 A. ($\varepsilon_{max.}$ 30,000) in accord with the assigned structure. Treatment with Brady's reagent in the cold gave a product capable of separation into two fractions: (A), soluble in ethyl acetate from which it separated as long cherry-red needles, m. p. 215—217° (rapid heating) (Found : C, 63·3; H, 6·0; N, 14·5. $C_{20}H_{22}O_4N_4$ requires C, 62·8; H, 5·8; N, 14·7%); and (B), only slightly soluble in ethyl acetate, crystallised from ethyl acetate–toluene as dark purple needles, m. p. 254—255° (Found : C, 63·1; H, 5·7; N, 14·8%). They are probably syn- and anti-*forms* of the 2 : 4-*dinitrophenylhydrazone* of the above ketoanthracene; (A) showed absorption at $\lambda_{max.}$ 4000 (ε 32,300), 3150 (ε 9500), and 2650 A. (ε 17,500), and (B) absorbed at $\lambda_{max.}$ 3950 (ε 26,700), and 2590 A. (ε 14,700) (in chloroform). Compound (A), kept in ethyl acetate containing a little hydrochloric acid for a day, was transformed into (B).

The dodecahydrohydroxyketoanthracene, m. p. 178—184°, on treatment with alkali as above gave rise to the decahydroketoanthracene, m. p. 102—103°, in quantitative yield. The latter (0·269 g.) was reduced with sodium (1·71 g.) and ethanol (40 c.c.) and dehydrogenated with 25% palladium–charcoal (0·262 g.) at 300° for 3·5 hours. The product obtained by extraction with benzene and passage through alumina (25 g.) was anthracene (0·06 g.), m. p. 212—214° (trinitrobenzene complex, m. p. 163—164°), both m. p.s being undepressed by authentic specimens.

Disproportionation and Oxidation of 1 : 4 : 5 : 8-*Tetrahydro-2-methoxynaphthalene.*—The methoxytetralin (10 g.) was added to freshly prepared Raney nickel (*ca.* 1 c.c.) in ethanol (40 c.c.), with stirring. The mixture became warm and was refluxed for 30 minutes, then filtered, and the ethanol removed under reduced pressure. The residual oil in ethanol gave a picrate, whence aqueous ammonia (3%) afforded 2-methoxynaphthalene (1·3 g.), m. p. 70°. Most of the alcohol was removed from the filtrate, which was poured into aqueous ammonia and extracted with ether (100 c.c.). Removal of the solvent and distillation gave an oil, b. p. 122—126°/14 mm., which after being boiled with 3% sulphuric acid (10 minutes) gave a small amount of a crystalline bisulphite compound, decomposed by sodium carbonate to 1 : 2 : 3 : 4-tetrahydro-2-ketonaphthalene (0·3 g.). The material recovered after the bisulphite treatment was added to a solution of potassium amide (from the metal, 5 g.) in liquid ammonia (100 c.c.) with development of a deep red colour. Distillation of the product gave two fractions : (A) b. p. 90—

96°/14 mm., and (B) b. p. 135—138°/16 mm. Redistillation of (A) over sodium gave a colourless oil (2·0 g.), b. p. 208° (odour of tetralin), which is probably a mixture of dihydronaphthalenes (Found : C, 92·1; H, 7·9. Calc. for $C_{10}H_{10}$: C, 93·3; H, 7·7%). This corresponds to 1 : 2 : 3 : 4-tetrahydro-2-methoxynaphthalene (2·5 g.) in the original disproportionation product. Fraction (B) (3·5 g.) was oxidised with chromic acid (Stork, *loc. cit.*) to 1 : 2 : 3 : 4-tetrahydro-1-keto-6-methoxynaphthalene, m. p. 79°, and is therefore 1 : 2 : 3 : 4-tetrahydro-6-methoxynaphthalene.

To a stirred solution of 1 : 4 : 5 : 8-tetrahydro-2-methoxynaphthalene (2·97 g.) in dry benzene (20 c.c.) was slowly added lead tetra-acetate (8·1 g.) with cooling in water. After 15 minutes the lead acetate was removed by filtration and the product distilled (2·04 g.; b. p. 86—100°/1 mm.). It was heated with 2N-sulphuric acid (20 c.c.) under nitrogen for 15 minutes, taken up in ether, and shaken with saturated aqueous sodium hydrogen sulphite for 3 hours. A small amount of the bisulphite derivative of 1 : 2 : 3 : 4-tetrahydro-2-ketonaphthalene was removed by filtration, and gave after decomposition with sodium carbonate the ketone (*ca.* 60 mg.). The residual oil was dissolved in light petroleum (b. p. 40—60°) and cooled in carbon dioxide–acetone, to yield 2-methoxynaphthalene (0·4 g.), m. p. 70°. The action of bromine in carbon tetrachloride on the light petroleum solution gave 2 : 3-dibromo-1 : 4-dihydro-6-methoxynaphthalene, m. p. 97° (cf. Beer, *loc. cit.*) (Found : C, 41·3; H, 3·9. Calc. for $C_{11}H_{12}OBr_2$: C, 41·2; H, 3·75%).

1 : 4-*Dihydro*-5-2′-*hydroxyethoxynaphthalene* (XV).—1-2′-Hydroxyethoxynaphthalene (30 g.; b. p. 194—196°/15 mm.) in methanol (36 c.c.) and ammonia (200 c.c.) was reduced with sodium (13 g.). Distillation of the product gave a viscous oil (26 g.), b. p. 138—142°/0·3 mm., which solidified to give 1 : 4-*dihydro*-5-2′-*hydroxyethoxynaphthalene*, long needles (from light petroleum, b. p. 40—60°), m. p. 56° (Found : C, 75·8; H, 7·6. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%). In an endeavour to produce more profound reduction the hydroxyethoxynaphthalene (10 g.) was treated in methanol (31 c.c.) and ammonia (200 c.c.) with sodium (12 g.). Worked up in the usual way, the product gave the following fractions: (A), b. p. 80—85°/20 mm. (1·5 g.); (B), b. p. 152—160°/18 mm. (4·6 g.); and (C), b. p. 160—184°/18 mm. (2·6 g.). Fraction (A) partly solidified to give 1 : 4 : 5 : 8-tetrahydronaphthalene, m. p. 42°, and from (C) was obtained crystalline 1 : 4-dihydro-5-2′-hydroxyethoxynaphthalene (1·2 g.), m. p. 56°. Fraction (B) with cold Brady's reagent gave mixed 2 : 4-dinitrophenylhydrazones, m. p. 175—200°, which were fractionally crystallised from benzene–light petroleum (b. p. 40—60°) to give what appear to be three distinct *compounds* : (D), bright red needles, m. p. 238° (Found : C, 58·6; H, 5·3; N, 17·55. $C_{16}H_{16}O_4N_4$ requires C, 58·6; H, 4·9; N, 17·1%); (E), orange plates, m. p. 152—155° (Found : C, 59·0; H, 5·4; N, 17·2%); and (F), orange-yellow plates, m. p. 144° (Found : C, 58·1; H, 5·2; N, 17·2%). Both (E) and (F) were converted into (D) by hot alcoholic sulphuric acid, and the three compounds are probably bond-isomers. Attempts to isolate a uniform ketone after acid hydrolysis of (B) were unsuccessful. Heating with sulphuric acid (10%) under reflux in nitrogen for 10 minutes afforded a mixture, b. p. 110—145°/10 mm., giving a mixed derivative, m. p. 180—200°, with 2 : 4-dinitrophenylhydrazine; after the fraction (B) had been shaken in ethyl acetate solution for 30 minutes with aqueous sulphuric acid at pH 4 a *product*, possibly mainly a cyclic acetal, was isolated, having b. p. 132°/16 mm. (Found : C, 74·3; H, 8·7. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%); it showed an ill-defined inflection at 2240—2330 A.

Reduction of 1 : 2 : 3 : 4-*Tetrahydro*-5-2′-*hydroxyethoxynaphthalene*.—1 : 2 : 3 : 4-*Tetrahydro*-5-2′-*hydroxyethoxynaphthalene* was made in the standard manner from 1 : 2 : 3 : 4-tetrahydro-5-hydroxynaphthalene by the action of an excess of ethylene chlorohydrin and aqueous alkali. It had b. p. 143°/0·25 mm., m. p. 52° [from light petroleum (b. p. 40—60°)] (Found : C, 75·0; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). The ether (15 g.) in ethanol (25 c.c.) was added to ammonia (250 c.c.) and reduced with sodium (10 g.). Distillation of the product gave (A) (*ca.* 1 g.), b. p. 90°/10 mm., and (B) (11·5 g.), b. p. 135—140°/0·2 mm. Fraction (A) after re-distillation over sodium had b. p. 203—204°, n_D^{18} 1·5162, and appeared to be a hydrocarbon mixture. Fraction (B) was refluxed with 0·5N-sulphuric acid for an hour, and the product taken up in ether and distilled (b. p. 120—140°; 5 g.). A small residue from the distillation crystallised and proved to be unchanged starting material. Redistillation gave two fractions : (C), (0·9 g.) b. p. 120—123°/13 mm., and (D), b. p. 134—136°/13 mm. (3·9 g.). Fraction (C) on treatment with sodium hydrogen sulphite solution gave a small amount of the derivative of decahydro-1-ketonaphthalene; fraction (D) was 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-1-ketonaphthalene (Found : C, 80·4; H, 9·4. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·4%). The 2 : 4-dinitrophenylhydrazone had m. p. 262° (Found : N, 16·5. Calc. for $C_{16}H_{10}O_4N_4$: N, 16·9%); its m. p. was undepressed by an authentic specimen.

Reduction 5 : 6 : 7 : 8-*Tetrahydro*-3-*methoxy*-2-*naphthoic acid*.—The dry sodium salt of 1 : 2 : 3 : 4-tetrahydro-6-hydroxynaphthalene was heated to 190° for 2 hours in an atmosphere of carbon dioxide. The acid portion of the product was methylated by the repeated action of methyl sulphate and sodium hydroxide until a test portion on acidification produced a crystalline acid not giving a purple colour with ferric chloride. The 5 : 6 : 7 : 8-*tetrahydro*-3-*methoxy*-2-*naphthoic acid*, precipitated on acidification of the solution, crystallised from aqueous acetic acid as long prisms, m. p. 115° (Found : C, 70·0; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). To form its sodium salt the acid (5 g.) was added to the product from sodium (0·6 g.) and ethanol (30 c.c.) in ammonia (300 c.c.), and reduction was carried out by addition of sodium (6 g.) in small pieces. After addition of water (150 c.c.) most of the ammonia was removed under reduced pressure; ether-extraction of the solution gave no product. Acidification to Congo-red paper gave an oil and, on boiling, carbon dioxide was evolved. The oil was taken up in ether and separated into fractions soluble and insoluble in aqueous sodium carbonate. The neutral fraction (0·8 g.) had b. p. 120—135°/11 mm. On treatment with aqueous sodium hydrogen sulphite it gave a crystalline solid (A) and unchanged oil (B). The adduct (A) was decomposed by shaking it with dilute hydrochloric acid and ether for an hour. The resulting small amount of pleasant-smelling oil gave 1 : 2 : 3 : 4 : 5 : 6 : 7 : 10-*octahydro*-6-*ketonaphthalene* 2 : 4-*dinitrophenylhydrazone*, m. p. 134—135° (Found : C, 57·7; H, 5·3. $C_{16}H_{16}O_4N_4$ requires C, 58·2; H, 5·4%). The formulation is based on the orange-yellow colour of the derivative, and the fact that by alcoholic sulphuric acid it was converted into the derivative, m. p. 188—189°, of (B). Fraction (B), b. p. 125—128°/14 mm., gave 1 : 2 : 3 : 4 : 5 : 6 : 9 : 10-*octahydro*-6-*ketonaphthalene* 2 : 4-*dinitrophenylhydrazone* as dark red prisms, m. p. 188—189° (Found : C, 58·3; H, 5·4%).

Reduction of 5 : 6 : 7 : 8-*Tetrahydro*-1-*methoxy*-2-*naphthoic acid.*—The acid was prepared as above, starting from 1 : 2 : 3 : 4-tetrahydro-5-naphthol; methylation of the hydroxy-acid required a very large excess of methyl sulphate. 5 : 6 : 7 : 8-*Tetrahydro*-1-*methoxy*-2-*naphthoic acid* formed prisms (from aqueous acetic acid), m. p. 116—117° (Found : C 70·1; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). Reduced as above, the acid (10 g.) gave a neutral fraction (0·7 g.), b. p. 115—125°/14 mm. This partly crystallised in the refrigerator, and crystallised from light petroleum (b. p. 40—60°) as prisms, m. p. 72—73°, which appear to be 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*octahydro*-5-*ketonaphthalene* (Found : C, 79·5; 9·1. $C_{10}H_{14}O$ requires C, 80·0; H, 9·35%). The 2 : 4-*dinitrophenylhydrazone* formed bright red prisms (from ethyl acetate), m. p. 207° (Found : C, 57·8; H, 5·3. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·4%). The acid fraction from the reduction was a thick oil (7·6 g.) which was oxidised in acetic acid (20 c.c.) by chromium trioxide (3 g.) in water. After the exothermic reaction was complete, addition of water gave a white solid which crystallised from aqueous acetic acid as long needles, m. p. 142° undepressed by an authentic specimen of 1 : 2 : 3 : 4-tetrahydro-6-naphthoic acid.

Ultra-violet and infra-red absorption spectra are by Dr. F. B. Strauss (Oxford) and Dr. R. N. Haszeldine (Cambridge).

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