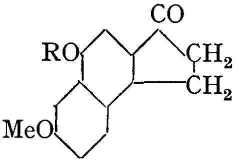
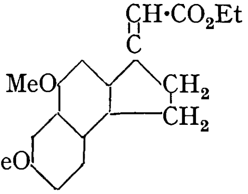
76. *Experiments on the Synthesis of Substances related to the Sterols. Part XXXIII. Hydrogenation of some* cyclo*Pentenonaphthalene Derivatives.*

By L. C. Bateman and Sir Robert Robinson.

The experiments described in Part XXX (Robinson and Weygand, this vol., p. 386) establish the possibility of the synthesis of testosterone, or close analogues, provided the requisite tricyclic ketones can be obtained. One promising way of securing such intermediates is by modification of *cyclo*pentenonaphthalenes, made in the first instance by the general method adumbrated in Part XXI (Robinson, J., 1938, 1390). For the purpose in view *p*-methoxyacetophenone is the appropriate starting point and this ketone has been transformed by way of the usual steps into 3'-*keto*-4-*acetoxy*-6-*methoxy*-1 : 2-cyclo*pentenonaphthalene* (I, R = Ac).

(I.)

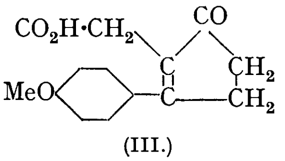




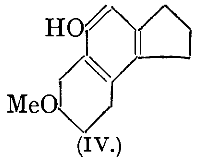
(II.)

The behaviour of this substance on catalytic hydrogenation has thrown some light on the reduction stages to be expected. Under the conditions employed, the carbonyl oxygen was eliminated and the terminal aromatic nucleus was reduced; one product was a hydrocarbon the constitution of which is discussed below. Taking advantage of the work of Robinson and Slater (Part XXIX, this vol., p. 376) in the *cyclo*pentenophenanthrene series, we submitted the *dimethoxy*-compound (I, R = Me) to the Reformatzky reaction, and the *product* (II, with ethyl bromoacetate) has been hydrogenated. The results are parallel with those observed in the reduction of (I) and differ from those obtained in the work recorded in Part XXIX. Further investigation of the constitution of all these hydrogenation products, including those of the tetracyclic series, is in progress.

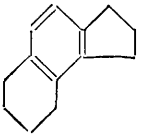
4 : 7-Diketo-7-*p*-methoxyphenylheptoic acid (Robinson and Todd, J., 1939, 1745) is readily converted in hot alkaline solution into 3-p-*methoxyphenyl*-Δ^2-cyclo*penten*-1-*one*-2-*acetic acid* (III). The cyclisation of the corresponding phenyl*cyclo*pentenoneacetic acid was accomplished in poor yield by means of sulphuric acid (Robinson, *loc. cit.*), but we now find that boiling acetic anhydride may be used as condensing agent in the case of (III) (and doubtless for the simpler acid also). The reaction is by no means so facile as in the naphthyl*cyclo*pentenoneacetic acid series and at first we employed propionic anhydride for the sake of the higher boiling point. Later it was found that acetic anhydride in a sealed vessel at 170—190° was equally, if not more, satisfactory; the product is (I, R = Ac). Hydrogenation in the presence of Raney nickel at elevated temperature and pressure was accomplished in alcoholic solution and two products were isolated. The first was a crystalline *substance*, $C_{14}H_{18}O_2$. This contained a methoxyl group and a phenolic hydroxyl (azo-compound with diazotised *p*-nitroaniline); it is therefore (IV).



(III.)



(IV.)



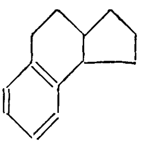
(V.)

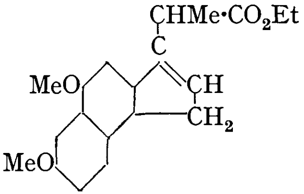
The second product was a liquid *hydrocarbon*, $C_{13}H_{16}$, which was not obtained quite pure (*ca.* 1% OMe). The alternative 1 : 2 : 3 : 4-tetrahydro-1 : 2-*cyclo*pentenonaphthalene *

---

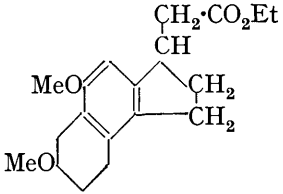
* The hydrocarbon was described as 1 : 2-*cyclo*pentano-1 : 2 : 3 : 4-tetrahydronaphthalene, but it is a tetrahydro-derivative of *cyclo*pentenonaphthalene and the change from " eno " to " ano " is thus superfluous and indeed misleading, as it suggests a hexahydro-derivative. This confusion is avoided by regarding *cyclo*pentenonaphthalene as the reference substance instead of tetrahydronaphthalene and the hydrocarbon is then named as in the text.

(VI) has been synthesised by Kon (J., **1933**, 1085) by an unambiguous method. Its b. p. is much lower than that of our hydrocarbon, although, as might be expected, the refractive powers are almost identical and very different from those of 1 : 2-*cyclo*pentenonaphthalene on the one hand and its more fully reduced derivatives on the other.


(VI.)



(VII.)



(VIII.)

There exist, therefore, independent reasons for the assumption that the central nucleus is the more resistant to hydrogenation in the course of formation of both (IV) and (V), though naturally the argument for the constitution (IV) reinforces that for (V) and *vice versa*, because there can be little doubt but that (V) is obtained by way of (IV).

Although these results are of interest in connexion with the mechanism of hydrogenation, our synthetical objective demands the retention of a reactive group in or near the *cyclo*pentane ring. We therefore applied the Reformatzky reaction to 3′-*keto*-4 : 6-*dimethoxy*-1 : 2-cyclo*pentenonaphthalene* (I, R = Me) and obtained directly unsaturated esters. That from ethyl bromoacetate is *yellow* (cf. Robinson and Slater, *loc. cit.*) and is considered to be represented by (II); the *methyl* derivative, from ethyl α-bromopropionate, is, however, *colourless* and is considered to be (VII). The latter ester is smoothly hydrolysed by aqueous alcoholic alkali, whereas the former, though attacked by the reagent, behaves differently and the corresponding acid has not yet been isolated.

The pressure hydrogenation of (II) furnished as the main product a crystalline mixture of hexahydro-derivatives, one of which was isolated by fractional crystallisation. Stereoisomerism is possible whatever formula is attributed to this substance. In view of the conclusions reached in the case of the reduction products of the ketone (I, R = Ac) we provisionally regard this substance as having the constitution (VIII). Experiments are in hand with the object of definitely settling this point, which is important for the planning of an extension of the investigation.

In addition a relatively smaller quantity of a demethoxy-derivative of (VIII) was obtained. On demethylation this gave a phenol (azo-coupling) and therefore the surviving methoxyl is a substituent in an unreduced aromatic nucleus. The constitution is probably (VIII) with the methoxyl in position 6 replaced by hydrogen.

EXPERIMENTAL.

Derivatives of 4 : 7-*Diketo*-7-p-*methoxyphenylheptoic Acid.*—Treatment of the acid (1 mol.) with 2 : 4-dinitrophenylhydrazine (2·1 mols.) in hot acetic acid afforded the *mono*-2 : 4-*dinitrophenylhydrazone*, orange microscopic crystals, m. p. 163—165° (decomp.) (Found : N, 13·5. $C_{20}H_{20}O_8N_4$ requires N, 12·7%). Similarly, treatment with semicarbazide hydrochloride (2·1 mols.) in aqueous sodium carbonate solution, followed by acidification with acetic acid, afforded the *monosemicarbazone*, a white crystalline powder, m. p. 166° (decomp.) (Found : N, 12·8. $C_{15}H_{19}O_5N_3$ requires N, 13·0%). Other diketoarylheptoic acids give bis-derivatives (cf. Part XXI, J., 1938, 1394), so this is an example of the relative inactivation of a carbonyl group in the " neutralised " system of the anisoyl group.

3-p-*Methoxyphenyl*-Δ^2-cyclo*penten*-1-*one*-2-*acetic Acid* (III).—This acid was obtained by following exactly the method for the corresponding phenyl derivative (J., 1938, 1392). The crude substance was a buff-coloured powder, m. p. 131°, which was employed in the next stage. The *acid* was crystallised from chilled acetone and then twice from benzene, being obtained in white feathery needles, m. p. 133° (Found : C, 68·1; H, 5·7. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%). Crystallisation from water gave a *hydrate* in long, transparent needles (up to 2 ins.) (Found : C, 63·0; H, 6·1. $C_{14}H_{14}O_4,H_2O$ requires C, 63·7; H, 6·1%). The general properties of this acid are similar to those of related substances already described.

4-*Hydroxy*-3′-*keto*-6-*methoxy*-1 : 2-cyclo*pentenonaphthalene* (I, R = H) *and its Derivatives.*—The acetyl derivative (below) was hydrolysed by means of aqueous alcoholic sodium hydroxide, and the yellow solution acidified. The precipitated *keto-phenol* crystallised from *iso*amyl alcohol in soft, flat, yellow plates, m. p. 250—255° to a black tar, after darkening from *ca.* 235° (Found: C, 73·8; H, 5·4. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%).

The *acetyl* derivative (I, R = Ac) was obtained by heating a mixture of *p*-methoxyphenyl*cyclo*pentenoneacetic acid (15 g., crude) and acetic anhydride (80 c.c.) in a sealed bulb at 170—190° for 1·5—1·75 hours. The solution was cooled rapidly with shaking in order to get small crystals (which do not occlude so much of a dark colouring matter as the larger nodules formed on slow cooling), and the light brown powder was collected, washed with a little acetic anhydride and then light petroleum, and dried (14·0 g.). One crystallisation from dioxan gave pale yellow, soft needles (10·0 g.), m. p. 193—194°. A small specimen was crystallised successively from aqueous acetic acid, ethyl alcohol, and methyl alcohol, forming white needles, m. p. 194° (Found: C, 71·2; H, 5·3. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%). The yellow solution in sulphuric acid exhibits a strong blue fluorescence. This derivative is formed by simply refluxing the acid with acetic anhydride, but the yields are not satisfactory (2 g. of the acid with 10 c.c. of acetic anhydride, refluxed for 3 hours, gave 0·6 g. of crude product; the filtrate with 4 c.c. more acetic anhydride, refluxed for 8 hours, gave 0·95 g. more of the crude material; with twice the amount of acetic anhydride the yield was 1·15 g. and these products were badly discoloured).

The *acetate* of the oxime of the acetyl derivative was obtained as follows: The oxime of the acetyl derivative, prepared by the action of hydroxylamine hydrochloride and pyridine at 95°, separated from aqueous pyridine as a buff, crystalline powder; on heating, it darkened at about 210° and decomposed to a dark tar at about 230°. As some deacetylation was suspected, the derivative was heated with acetic anhydride until a clear solution resulted. The recovered derivative crystallised from ethyl acetate in fine, shiny, white needles, m. p. 196° (decomp.) with previous darkening (Found: C, 65·9; H, 5·1; N, 4·2. $C_{18}H_{17}O_5N$ requires C, 66·0; H, 5·2; N, 4·3. $C_{16}H_{15}O_4N$ requires C, 67·4; H, 5·3; N, 4·9%). The substance has, therefore, the composition of a diacetate of the oxime of (I, R = H).

The *propionyl* derivative (I, R = COEt) was obtained by refluxing a mixture of *p*-methoxyphenyl*cyclo*pentenoneacetic acid (2 g.) and propionic anhydride (10 c.c.) for 1 hour. The crystalline product obtained on cooling was collected (1·3 g.). Crystallisation from methyl alcohol gave yellow needles (1·0 g.) and on several recrystallisations, white feathery needles, m. p. 160° (Found: C, 71·7; H, 5·6. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%).

The *methyl* ether (I, R = Me) was obtained in the usual manner by combined hydrolysis and methylation of the acetyl derivative by means of aqueous alcoholic potassium hydroxide and methyl sulphate. It crystallised from *iso*amyl alcohol in soft, shiny, pale greenish-yellow needles, m. p. 156° (Found: C, 74·2; H, 5·8; OMe, 24·8. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8; 2OMe, 25·6%).

The *oxime* of the methyl ether, prepared by the pyridine method, separated from aqueous pyridine in pale yellow crystals, m. p. 235—236° (decomp.); recrystallisation from *iso*amyl alcohol–ethyl alcohol gave soft, shiny, white plates, m. p. 236° (decomp.) (Found: N, 5·2. $C_{15}H_{15}O_3N$ requires N, 5·4%).

Hydrogenation of 3'-*Keto*-4-*acetoxy*-6-*methoxy*-1 : 2-cyclo*pentenonaphthalene*.—A mixture of the acetyl compound (5·5 g.), Raney nickel (1 g.), and alcohol (500 c.c.) was stirred with hydrogen under 95—100 atms. initial pressure. The autoclave was heated to 130—135° in the course of 2½ hours and kept at 135—145° for 3 hours longer. After cooling, the solvent was evaporated from the centrifuged and filtered solution under diminished pressure. The residual greenish oil was taken up in light petroleum (b. p. 60—80°), and the filtered solution allowed to evaporate at room temperature. As nothing crystallised, the oil was again dissolved in light petroleum (40 c.c., b. p. 60—80°), and the solution dried, filtered, and kept for 12 hours in the refrigerator; *ca.* 0·5 c.c. of a yellow oil (A) separated. No further separation occurred from the decanted solution, kept in the refrigerator for 12 hours, but, on stirring and scratching, a white solid (B) (0·5 g. after 2 days) crystallised. The filtrate was evaporated (*ca.* 3 c.c. of residue) and distilled. The first fraction (*ca.* 0·5 c.c.), b. p. 120—125°/0·3 mm., $n_D^{15°}$ 1·5542, was a clear, colourless oil (Found: C, 89·6; H, 9·8; OMe, 1·0. $C_{13}H_{16}$ requires C, 90·7; H, 9·3%. $C_{13}H_{14}$ requires C, 91·8; H, 8·2%. $C_{13}H_{18}$ requires C, 89·6; H, 10·4%). (A mixture of 94% of $C_{13}H_{16}$ with 6% of $C_{13}H_{21}$·OMe requires C, 89·9; H, 9·5; OMe, 1·0%.) For the reasons stated in the introduction this hydrocarbon, $C_{13}H_{16}$, is probably 5 : 6 : 7 : 8-*tetrahydro*-1 : 2-cyclo*pentenonaphthalene* (V). The 1 : 2 : 3 : 4-tetrahydro-isomeride is described by Kon (*loc. cit.*) as having b. p. 138°/19 mm. and n_D 1·55297. Decahydro*cyclo*pentenonaphthalene has b. p. 71—72°/2·5 mm., $n_D^{20°}$ 1·4895 and the $\Delta^{9:10}$-octahydro-derivative has b. p. 74—76°/3 mm., $n_D^{20°}$ 1·5074 (Pinkney, Nesty, Wiley, and Marvel, *J. Amer. Chem. Soc.*, 1936, **58**, 972); 1 : 2-*cyclo*pentenonaphthalene has b. p. 118°/0·5 mm., b. p. 170°/15 mm., n_D 1·6265—1·629 (Kon, *loc. cit.*; Cook and Hewett, J., **1933**, 1098; Kruber, *Ber.*, 1932, **65**, 1382). The refractive power is therefore strong confirmatory evidence of the formula $C_{13}H_{16}$. The b. p. of our hydrocarbon is almost the same as that of *cyclo*pentenonaphthalene and therefore the aromatic nature of the central nucleus is the controlling factor. It is easy to see that this must also govern the molecular shape and both *cyclo*pentenonaphthalene and its 5 : 6 : 7 : 8-tetrahydro-derivative will be sensibly flat molecules. In confirmation naphthalene has b. p. 218°/760 mm. and tetrahydronaphthalene, b. p. 206°/720 mm., and it is well known that benzene and *cyclo*hexane have about the same b. p.'s.

A second fraction (*ca.* 2 c.c.) from the distillation had b. p. 125—145°/0·3 mm. (Found : C, 84·5; H, 9·2; OMe, 9·1%) and the residue in the flask was a viscous, yellow syrup.

The yellow oil (A) partly crystallised on keeping and by trituration with light petroleum (b. p. 60—80°) and eventual crystallisation from this solvent, the m. p. was raised to 122—123° and then to 126—127°. The crystals (B), recrystallised four times from benzene–light petroleum, gave small, hard, colourless rhombs (0·2 g.), m. p. 126—127° (Found : C, 76·7; H, 8·1; OMe, 14·0. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·2; 1OMe, 14·2%). This substance is cryptophenolic; it gives no coloration with ferric chloride in alcoholic solution and it is not soluble in aqueous sodium hydroxide. When it was heated with chloroform and alcoholic potassium hydroxide in the presence of a little copper bronze, a pink colour was developed. The isolated product now gave a bluish-green colour with alcoholic ferric chloride. The substance $C_{14}H_{18}O_2$ is, however, most easily recognised as a phenol by azo-coupling. It slowly coupled with diazobenzenesulphonic acid in acetic acid solution in the presence of sodium acetate to an orange-yellow azo-compound : the reaction was much more rapid and complete in alcoholic solution. This azo-compound dissolved in aqueous sodium hydroxide to a bluish-red solution. An immediate reaction occurred in alcoholic solution with *p*-nitrobenzenediazonium acetate; the *product* crystallised from aqueous acetic acid or alcohol in soft, slender, brownish needles with a weak golden lustre, m. p. 173° (Found : N, 12·0. $C_{20}H_{21}O_4N_3$ requires N, 11·5%). The solution in aqueous sodium hydroxide had a deep indigo-blue colour. The possibility that a methoxyl group was extruded in this coupling was entertained and dismissed because there was no evidence of such a reaction with diazotised *p*-nitroaniline among analogous compounds known to be fully methylated and because the hydrolysis of methoxyl has not been observed with diazobenzenesulphonic acid under conditions similar to those mentioned above.

The products of a second hydrogenation carried out on a slightly larger scale (6 g.) were hydrolysed by means of aqueous alcoholic potassium hydroxide in order to ensure the removal of acetoxyl groups. After isolation two fractions were obtained on distillation, b. p. 140—180°/1 mm. and b. p. 180—200°/1 mm. The first fraction, a faintly yellow oil, partly crystallised : the solid was collected after addition of light petroleum; it had m. p. 116—119° and, after several recrystallisations, m. p. 126—127°; the first filtrate was inadvertently lost and this should have contained the hydrocarbon $C_{13}H_{16}$. The mother-liquors from the crystallisations contained an uncrystallisable oil (Found : OMe, 12·2%). The second fraction, a viscous yellow syrup, slowly solidified to hard, white rosettes, m. p. 103—110° after being washed with light petroleum. Recrystallisation raised the m. p. to 125—126° and then to 126—127°, undepressed by admixture with the specimen from the first experiment.

Hydrogenation of 3′-*Oximino*-4 : 6-*dimethoxy*-1 : 2-cyclo*pentenonaphthalene. Formation of* 4 : 6-*Dimethoxy*-1 : 2-cyclo*pentenonaphthalene.*—This experiment was undertaken in the hope that nuclear reduction would occur and that a point of attack might be secured in the form of an amino-group in the *cyclo*pentane ring. The outcome, however, was that the ketoxime group was reduced to methylene and the aromatic nuclei were unaffected.

The oxime of ketodimethoxy*cyclo*pentenonaphthalene (8·2 g.) and Raney nickel (2 g.) were shaken with dioxan (250 c.c.) under hydrogen at an initial pressure of 100 atms. The temperature was raised to 100° during an hour, to 160° during 2 further hours, and then maintained at 190—200° for 3 hours. The cooled product had a strong ammoniacal odour. Isolated in the usual way, the *product* was a white wax which contained only traces of nitrogen. It was readily soluble in the common organic solvents with the exception of methyl alcohol and light petroleum. It was triturated with a little cold methyl alcohol, collected, and dried (5 g., m. p. 81—82°) (Found : C, 78·7; H, 6·5. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·0; 2OMe, 27·2%). Recrystallisation from light petroleum and aqueous methyl alcohol gave white plates, m. p. 84—85° (Found : C, 78·2; H, 7·1; OMe, 26·8%). The *picrate* separated in dull mauve crystals, m. p. 164—165°, from aqueous acetic acid (Found : N, 8·9. $C_{15}H_{16}O_2,C_6H_3O_7N_3$ requires N, 9·0%).

4 : 6-*Dimethoxy*-3′-iso*propylidene*-1 : 2-cyclo*pentenonaphthalene.*—As the yield in the process adopted was unsatisfactory, a detailed description would serve no useful purpose. An ethereal solution of *iso*propylmagnesium bromide was concentrated and mixed with anisole, and a solution of ketodimethoxy*cyclo*pentenonaphthalene in warm anisole introduced. The mixture was heated at 80°. On working up, a small quantity of a colourless substance was isolated. This crystallised from aqueous alcohol in slender, small, white, woolly needles, m. p. 98—99° (Found : C, 79·9; H, 7·3. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%).

4 : 6-*Dimethoxy*-3′-(*carbethoxymethylene*)-1 : 2-cyclo*pentenonaphthalene* (II).—A mixture of ketodimethoxy*cyclo*pentenonaphthalene (5·0 g.), ethyl bromoacetate (6·8 g., dried over potassium carbonate and distilled, b. p. 159·0—159·8°/768 mm.), zinc ribbon (2·6 g.), and dry benzene (70 c.c.) was refluxed with exclusion of moisture. After 20—30 minutes the zinc was seen to be attacked, and after 1·5 hours the liquid suddenly became opaque and thickened within a minute to a paste. Heating was continued for 30 minutes longer. The colour during the progress of the reaction gradually became deep brick-red. After cooling, ice and dilute sulphuric acid were added; the washed and dried benzene layer on evaporation left a dark red oil which solidified to an orange-red mass. This was washed with alcohol and light petroleum and dried (6·5 g., m. p. 150—155°). Two crystallisations from alcohol (*ca.* 300 c.c.) raised the m. p. to 158—159° and two more from aqueous dioxan gave orange-yellow needles, m. p. 162—163° (Found : C, 72·8; H, 6·4. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·4%) (91% of the theoretical * amount of silver iodide, from 2OMe and 1OEt, was obtained in a Zeisel determination). The solution of the ester in sulphuric acid is intensely red. The action of aqueous alcoholic potassium hydroxide on this ester gives an alkali-soluble product after ½ hour's refluxing, but the acid obtained is colloidal, hard to coagulate, and forms emulsions with ether and benzene. It has not been possible to purify it, and the indications are that some side reaction has occurred, possibly polymerisation. This behaviour is in marked contrast to that of the homologous ester described below.

4 : 6-*Dimethoxy*-3′-(α-*carbethoxyethyl*)-1 : 2-cyclo*pentadienonaphthalene* (VII).—A mixture of ketodimethoxy*cyclo*pentenonaphthalene (1·25 g.), ethyl α-bromopropionate (3·8 g., b. p. 57—59°/17 mm.), zinc ribbon (1·3 g.), and dry benzene (35 c.c.) was refluxed. After 45 minutes a pale brown, gelatinous mass had separated and the heating was continued for 30 minutes longer. The product, isolated as in the case of the lower homologues, formed a red syrup; this was taken up in light petroleum (75 c.c.), and the solution filtered from a small brown precipitate. The solvent was removed, the residue dissolved in a little alcohol, and water added to produce an incipient clouding of the hot solution, which was then stirred with charcoal and filtered. On cooling, yellow crystals (1·1 g., m. p. 92°) separated. Three recrystallisations from aqueous alcohol gave white, woolly needles, m. p. 95° (Found : C, 72·9; H, 6·6. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·7%) (88·1% of the theoretical amount, from 2OMe and 1OEt, of silver iodide was obtained in a Zeisel determination). A deep red solution was formed in sulphuric acid.

The *ester* (0·65 g.) was hydrolysed by refluxing for ½ hour with potassium hydroxide (1 g.), water (10 c.c.), and alcohol (30 c.c.). After dilution and filtration, the *acid* was precipitated as a buff-coloured powder. It was purified by solution in aqueous sodium carbonate, reprecipitation after washing with ether, and by several crystallisations from methyl alcohol, being so obtained in transparent plates, m. p. 172° (Found : C, 72·6; H, 6·1. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·0%).

Hydrogenation of (II). *Formation of a Hexahydro-derivative* (*probably* VIII) *and Other Products.*—The ester (10·0 g.), dissolved in alcohol (500 c.c.), was heated and stirred under compressed hydrogen in the presence of Raney nickel. After 3 hours the temperature was 150° and the pressure 150 atms. After 1 hour more the temperature had risen to 180° and it was kept at 180—200° for another 15·5 hours. On cooling and opening the autoclave, an odour resembling that of acetaldehyde was noticed. The product was isolated as a dark red syrup, which was distilled. After a small colourless fraction, b. p. up to 140°/0·1 mm., which had the aldehyde-like odour, the main bulk (7·5 g.) had b. p. 140—190°/0·1 mm. This solidified as a soft, white mass, m. p. 45—50° (Found : C, 73·2; H, 8·4%. 5·201 Mg. gave 7·89 mg. of AgI). No ketonic reactions could be observed, the material did not form a picrate, and the solution in sulphuric acid was yellow, becoming red on heating. The last drop of distillate in the flask gave a solid, m. p. 61—62°, and the residue in the flask was a black tar (A).

A portion of the main product, m. p. 45—50°, was crystallised several times from light

---

* Low results were obtained in all such experiments in the case of these methoxy-esters. In view of the possibility of *C*-methylation by migration and incomplete conversion of ethyl alcohol into ethyl iodide, the Zeisel estimation must be regarded as a study of yield rather than as a precise analysis that can be trusted blindly.

petroleum, the m. p. rising to 61—63°, 66·5—67·5°, 70—71°, 72·5—73°, 74·5—75·5°, 77—77·5°, 81—81·5°, 82—83°, 83—83·5°. The last fraction consisted of hard, white aggregates of flat prisms (Found : C, 71·4; H, 8·3. $C_{19}H_{26}O_4$ requires C, 71·7; H, 8·2%) (97% of the theoretical amount, from 2OMe and 1OEt, of silver iodide was obtained in a Zeisel determination). When a solution in light petroleum was quickly cooled, or evaporated, long, transparent, pointed, prismatic needles separated. Evaporation of a drop of the solution on a slide left structures filling the field of the microscope and consisting of many branched filaments rather like some of the algæ. This 4 : 6-*dimethoxy*-3′-(*carbethoxymethyl*)-5 : 6 : 7 : 8 (or 1 : 2 : 3 : 4)-*tetrahydro*-1 : 2-cyclo*pentenonaphthalene* has possibly been separated from a stereoisomeride. The product obtained after boiling with concentrated hydriodic acid and a few drops of acetic acid contains a true naphthol derivative, because it readily couples with diazobenzenesulphonic acid to a crimson azo-compound. Probably a dihydronaphthol is formed by hydrolysis and elimination of methyl alcohol and this suffers dismutation to the naphthol and tetrahydronaphthol.

The mother-liquors up to the fifth crystallisation were concentrated to 10 c.c. and kept in a refrigerator; the crystals that separated had m. p. *ca.* 45° (mother-liquor, B). These were recrystallised from light petroleum in two fractions, both of m. p. 66—67°; further crystallisation raised the m. p. to 70° and 73—74° (Found : C, 71·7; H, 8·2%. Yield of silver iodide, 96%). The mother-liquor (B) was evaporated; the residue could not be crystallised, and distilled as a pale yellow, very viscous syrup, b. p. 140—180°/0·1 mm. (Found : C, 73·5; H, 8·4. $C_{18}H_{24}O_3$ requires C, 75·0; H, 8·4%) (89·5% of the theoretical amount, for 1OMe and 1OEt, of silver iodide was obtained in a Zeisel determination). It is clear that this substance is essentially a *demethoxyhexahydro*-derivative, although it was by no means a pure specimen; on keeping, crystals appeared in the oil, but these were not further investigated. The acid corresponding to this ester is mentioned below.

The main product (2·3 g., m. p. 45—50°) was hydrolysed by refluxing for 1 hour with potassium hydroxide (5 g.), water (10 c.c.), and methyl alcohol (25 c.c.). The methyl alcohol was evaporated, and the residue thoroughly extracted with ether. On distillation of the residue (*ca.* 0·2 c.c.) after removal of the solvent at 0·02 mm. a clear, pale yellow oil was obtained, which set to an opaque resin on cooling (Found : C, 80·3; H, 10·0%). It is unlikely that the material is homogeneous, but it can contain only one oxygen atom in the molecule of the main constituent ($C_{14}H_{22}O$ requires C, 81·6; H, 10·5%. $C_{13}H_{20}O$ requires C, 81·3; H, 8·4%) unless it is derived from two molecules of the starting material ($C_{32}H_{50}O_3$ requires C, 79·7; H, 10·4%) ($C_{32}H_{50}O_3$ represents full reduction of the aromatic nuclei, elimination of one methoxyl from each component, reduction of the ester to a primary alcohol, and formation of an ether from two molecules). The aqueous alkaline solution afforded a pale yellow gum on acidification and this was extracted with boiling light petroleum (200 c.c., b.p. 60—80°), leaving a residue (C). On cooling, the solution deposited white crystals, m. p. 100—104°, and two recrystallisations gave white, hair-like needles, m. p. 117—118° (Found : C, 70·4; H, 7·6; OMe, 19·8. $C_{17}H_{22}O_4$ requires C, 70·3; H, 7·6; 2OMe, 21·4%). This *dimethoxy*(*carboxymethyl*)*tetrahydro*cyclo*pentenonaphthalene* (acid corresponding to VIII) was also obtained from the black tar (A), which was extracted with hot benzene (charcoal) and the solution diluted with light petroleum, filtered from a dark gelatinous precipitate, and evaporated to a dark syrup (1 c.c.). This was boiled with aqueous methyl-alcoholic potassium hydroxide, and the acid eventually isolated by means of ether as a biscuit-coloured powder, m. p. 94—100°. It was crystallised from benzene–light petroleum, methyl alcohol, and thrice from light petroleum (b. p. 60—80°) and obtained in white, feathery needles, m. p. 117—118° (Found : C, 70·5; H, 7·9; OMe, 20·1%).

The residue (C), after attempted crystallisation from benzene–light petroleum (removal of a little insoluble material), was distilled at 0·1 mm. (the b. p. could not be observed), and obtained as a clear yellow gum (*ca.* 0·5 g.) (Found : C, 73·2; H, 8·1; OMe, 11·2. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7; 1OMe, 11·9%). This acid, though not quite pure, is clearly a 4(or 6)-*methoxy*-3′-(*carboxymethyl*)*tetrahydro*cyclo*pentenonaphthalene* or a mixture of isomerides. An acid solution of diazobenzenesulphonic acid, to which sodium acetate had been added, was cautiously introduced into an alcoholic solution of the isolated product obtained on boiling this acid with hydriodic and acetic acids. The first result was the formation of a weak crimson coloration, indicating admixture with the acid, m. p. 117—118°. On shaking with alumina the dye was adsorbed and the very pale mauve filtrate on treatment with more of the diazo-solution gave an orange-coloured azo-compound, wine-red on addition of sodium hydroxide. This is strong evidence that the methoxy-group is a substituent in an aromatic nucleus. Hence it is the methoxyl contained in the reduced nucleus of the main product that is eliminated by further reduction.

Having by this experiment established the nature of the products of hydrogenation, we suggest that a simplified procedure would be to hydrolyse the crude material, remove neutral substances by extraction of the alkaline solution, and separate the acids by the method indicated above.

The authors thank the Department of Scientific and Industrial Research for a Senior Award (to L. C. B.).

DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, May* 28*th*, 1941.]