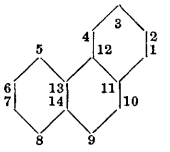
139. *Experiments on the Synthesis of Substances Related to the Sterols. Part XLV.*

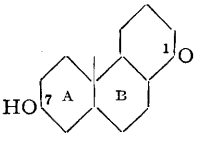
By J. W. Cornforth and (Sir) Robert Robinson.

The use of a naphthalene derivative to provide rings B and C of the sterol skeleton has advantages. In the investigation initiated by this memoir the ring A is added and a reactive group left in ring C which will facilitate the construction of ring D at a later stage.

The preparation of the tricyclic intermediate ABC is described and, making use of recognised analogies, it is pointed out that the stereochemical configuration is favourable apart from one dubiety.

The starting point is 1 : 6-dihydroxynaphthalene, and the tricyclic products may be endowed with various functional groups of which the most significant is perhaps the keto-alcohol (I).



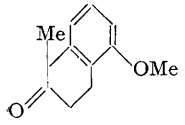


(I.)

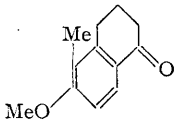
Evidence will shortly be submitted that the attempt of Martin and Robinson (*J.*, 1943, 497) to synthesise a stereoisomeride of androstendione broke down at the last stage, because the addition of a ring to the BCD intermediate did not proceed so as to give ABCD, which would have been structurally identical with androstendione, but afforded BCDE. Variations of this method are being studied in order to overcome the obstacle, *e.g.*, one in which the elements necessary for D are introduced but not developed into the cyclic ketone until A is added, and another in which the tricyclic intermediate (BCD) is not employed as heretofore as a diketone, but as a keto-alcohol. In any case the configurational aspects of this route are not sufficiently under control and for this reason we have devoted attention to another route, somewhat similar in character, but thought to be more precise stereochemically. It transpires that the new order of the stages has decided preparative advantages in addition.

The precedent researches are on the one hand those of Du Feu, McQuillin, and Robinson (Part XIV, *J.*, 1937, 53) and Robinson and Weygand (Part XXX, *J.*, 1941, 386) which showed that nascent methyl vinyl ketone (from the metho-salt of a methyl β-dialkylaminoethyl ketone) condenses with 2-methyl*cyclo*hexanone or with 1-methyl-2-decalone at the methine group bearing the methyl substituent in preference to the methylene group adjacent to carbonyl.

On the other hand the present authors have described a convenient method for the preparation of 2-tetralones from the 2-naphthols. In the course of this work (*J.*, 1942, 689) we mentioned the production of 5-methoxy-1-methyl-2-tetralone (II), isolated as the semicarbazone, from 6-methoxy-5-methyl-1-tetralone (III), which is the ketone used by Martin and Robinson (*loc. cit.*) as a starting point and prepared by them from β-naphthol.



(II.)



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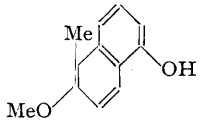

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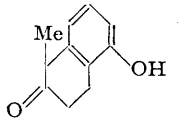

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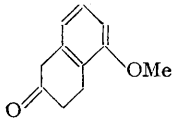
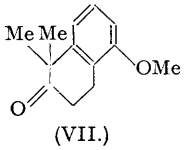


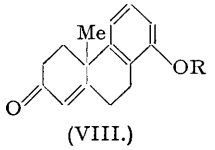
(VI.)

The preparation of II from III has been re-examined. 6-*Methoxy*-5-*methyl*-1-*naphthol* (IV) was isolated from the products of dehydrogenation of III with sulphur. The naphthol was reduced with sodium and alcohol, using a liquid ammonia medium (cf. Birch, *J.*, 1944, 434), and, after hydrolysis of the unstable enol ether, 5-hydroxy-1-methyl-2-tetralone (V) was obtained. This was readily methylated to II. The overall yield, though slightly better than before, was not encouraging.

In our previous communication (*loc. cit.*) we described the preparation of 5-methoxy-2-tetralone (VI) from 1 : 6-dihydroxynaphthalene. On methylation of VI with methyl iodide–sodium *iso*propoxide, the dimethylated ketone (VII) was the only product that could be isolated. We have now repeated, and have been able to improve, the preparation of VI. Since the production of VII in quantity indicates that the ketone (II) is unexpectedly reactive, we tried the methylation in methanol instead of in *iso*propanol, the object being to suppress the formation of anions from II. Under these conditions, a mixture of the ketones (VI), (VII), and (chiefly) (II) resulted. The separation of these might well have been difficult, but we found that II combines with sodium bisulphite slowly, whereas VI reacts quickly and VII not at all. Taking advantage of this observation, the isolation of the three ketones was easy. The identity of the ketone (II) with that previously prepared was established by comparison of the semicarbazones. This provides, incidentally, an additional proof of the structure of the α-tetralone (III).



(VII.)



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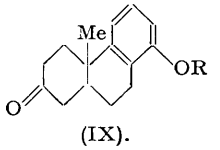
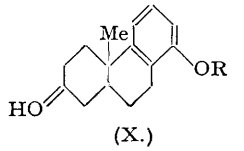


(IX).



(X.)

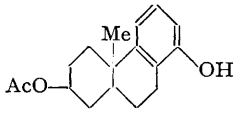
The unusually high acidity of II facilitated the preparation of a sodium enolate, a few minutes' treatment with sodamide in cold benzene being sufficient. Reaction of the enolate with 4-diethylaminobutan-2-one methiodide gave 7-*keto*-1-*methoxy*-13-*methyl*-5 : 6 : 7 : 9 : 10 : 13-*hexahydrophenanthrene* (VIII; R = Me) in 55% yield. We even expect to be able to improve this result, but it is already an unusually favourable case of this type of ring system extension.

The stepwise catalytic reduction of VIII (R = Me) in alcoholic solution gave successively 7-*keto*-1-*methoxy*-13-*methyl*-5 : 6 : 7 : 8 : 9 : 10 : 13_a: 14-*octahydrophenanthrene* (IX; R = Me) and 7-hydroxy-1-methoxy-13-methyl-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydrophenanthrene (X; R = Me). The latter was obtained as a mixture of epimers, one of which has been isolated in a pure condition. Dehydrogenation of X with selenium followed by demethylation gave 1-phenanthrol; a proof that the ring extension takes the direction illustrated in the formulae.

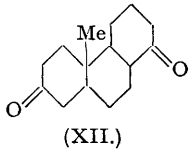
Demethylation of VIII (R = OMe) was effected rather smoothly by a dilute solution of hydrogen iodide in acetic acid. The resulting 1-*hydroxy*-7-*keto*-13-*methyl*-5 : 6 : 7 : 9 : 10 : 13-*hexahydrophenanthrene* (VIII; R = H) on reduction in neutral solution afforded 1-*hydroxy*-7-*keto*-13-*methyl*-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-*octahydrophenanthrene* (IX; R = H). This was isolated through the bisulphite compound: since it was thus obtained directly in a pure state, and no stereoisomeric ketone could be detected, it is very probable that the hydroaromatic rings are fused in the *cis*-form (cf. reductions of cholestenone and 2-keto-9-methyl-$\Delta^{1:10}$-octalin).

The reduction of IX (R = H) in acetic acid solution gave a mixture of epimers, but one predominated and was easily obtained pure. This 1 : 7-*dihydroxy*-13-*methyl*-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-*octahydrophenanthrene* (X; R = H) has probably, by analogy with the sterols, a *cis* relationship of the hydroxyl and angular methyl groups, and thus belongs to the *normal*, rather than the *epi*, series. The diol (X; R = H) was also obtained by direct reduction of VIII (R = H) and, though in poor yield, by demethylation of X (R = Me).

Treatment of the diol (X; R = H) with a slight excess of acetic anhydride, using potassium acetate as a catalyst and acetic acid as solvent, gave 1-*hydroxy*-7-*acetoxy*-13-*methyl*-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-*octahydrophenanthrene* (XI), the phenolic group remaining free. The monoacetate (XI) was hydrogenated over platinum in warm acetic acid, when hydrogen corresponding to three molecular proportions was absorbed. The product, without isolation, was oxidised with chromium trioxide in acetic acid and refluxed with alcoholic potash. The purpose of the latter operation was not only to remove the acetoxyl group, but also to rearrange any *cis*-α-decalones present to the *trans* form (cf. Hückel, *Annalen*, 1925, **441**, 1). The resulting product contained 7-hydroxy-1-keto-13-methyltetradecahydrophenanthrene (I) which was readily isolated as the sparingly soluble *semicarbazone*.



(XI.)



(XII.)

We have already expressed our view of the stereochemical relationship between carbon atoms 7, 13, and 14. As regards the positions 11 and 12, the method of preparation makes it probable that they are part of a *trans*-α-decalone; it is hard to decide which of the two possible *trans* forms would arise. It seems likely, therefore, that in the ketone (I) the five asymmetric carbon atoms have either the same relative configuration as is found in coprosterol, or the form, otherwise the same, in which rings B and C have the alternative linkage of the *trans* type.

In one experiment on the reduction of the phenolic ketone (VIII; R = H) with platinum and hydrogen, a small amount of neutral product was obtained. This was oxidised with chromic acid and converted into the 2 : 4-dinitrophenylhydrazone. From the resulting mixture (probably of mono- and bis-derivatives) a small quantity of a sparingly soluble derivative was isolated, which appeared to be the *bis*-2 : 4-*dinitrophenylhydrazone* of 1 : 7-*diketo*-13-*methyltetradecahydrophenanthrene*.

Experimental.

6-*Methoxy*-5-*methyl*-1-*naphthol* (IV).—6-Methoxy-5-methyl-1-tetralone (43 g.) was dehydrogenated with sulphur as previously described (*loc. cit.*). The product was treated with benzene and charcoal, and the naphthol extracted from the filtered solution with 2N-sodium hydroxide. The neutral fraction was again heated with sulphur and worked up as before. On acidification of the alkaline extracts the *naphthol* separated; it was purified by distillation [180° (bath temp.)/0·2 mm.] and crystallisation from benzene, giving 26 g., m. p. 138—141°. Another crystallisation from benzene gave colourless needles, m. p. 142—143° (Found: C, 76·3; H, 6·4. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%).

5-*Hydroxy*-1-*methyl*-2-*tetralone* (V).—The naphthol (IV) (40 g.) suspended in liquid ammonia (300 c.c.) and ethanol (27 c.c.) was reduced by the gradual addition of sodium (10·5 g.). When reaction was complete the solvent was removed and the residue dissolved in water (500 c.c.). (Passage of carbon dioxide at this point precipitated the enol ether, which crystallised from light petroleum in long needles, m. p. *ca.* 110°, but apparently had already suffered slight hydrolysis.) Hydrochloric acid was now added, sufficient to make the solution 1N with respect to it. A little benzene was added and the solution shaken for a short time, then cooled and treated with light petroleum (b. p. 40—60°). The product crystallised at once; it was collected next day, washed with water, then with benzene–light petroleum (1 : 2), dried, and extracted (Soxhlet) with light petroleum (b. p. 40—60°) for several hours. The residue (28 g.) then had m. p. about 120° with previous softening, and was used for the methylation. A sample recrystallised from benzene gave the *hydroxy-ketone* in aggregates of leaflets, m. p. 127—128° (Found: C, 75·0; H, 6·9. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%). This ketone did not afford a sodium bisulphite compound.

Methylation of 5-*Hydroxy*-1-*methyl*-2-*tetralone*.—The crude hydroxy-ketone (29·5 g.) was dissolved in sodium hydroxide

(10% excess of 2N) and shaken with methyl sulphate (5% excess), with gentle warming on the steam-bath. After 2 hours the cooled mixture was made strongly alkaline and extracted with ether. The ethereal solution was concentrated to about 60 c.c. and shaken with saturated sodium bisulphite solution (180 c.c.), for 9 hours. The solid additive compound began to separate after about an hour. It was collected, washed with ether, and decomposed by sodium carbonate in the presence of ether. The *methoxy-ketone* (II) distilled almost without residue at 102°/0·1 mm., as a colourless viscid oil (17 g.), $n_D^{16.5°}$ 1·5559 (Found: C, 75·4; H, 7·5. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%). The semicarbazone, crystallised from alcohol, had m. p. 188—190°, alone or mixed with an authentic specimen. From the ether washings of the bisulphite compound 2 : 5-dimethoxy-1-methylnaphthalene was recovered, m. p. 85° after crystallisation from alcohol. This of course arose from the naphthol (IV) which had escaped reduction in the previous stage.

Methylation of 5-Methoxy-2-tetralone (VI).—The ketone (9·7 g.; prepared in 70% overall yield from 1 : 6-dihydroxynaphthalene) was added to a solution of sodium (1·26 g.) in methanol (25 c.c.) under nitrogen. Methyl iodide (12 g.; 50% excess) was added at once with ice-cooling; the mixture was then allowed to warm spontaneously and finally refluxed for a few minutes. A few drops of dilute sulphuric acid were added and the nitrogen stream was stopped. Water was added and most of the methanol removed. The product was extracted with ether, and the ethereal solution concentrated to about 40 c.c. and shaken with small successive quantities of sodium bisulphite solution until the ethereal solution no longer gave the " tetralone-blue " reaction. The ether was then removed and the residue shaken overnight with fresh sodium bisulphite solution. The crystalline product from the last extraction was collected, washed well with ether, and decomposed with sodium carbonate, giving the monomethyl ketone (II) (3·65 g.), b. p. 102°/0·1 mm. The first sodium bisulphite washings, worked up in the same way, gave the unchanged ketone (VI) (2·4 g.). The ethereal solution of material which did not react with sodium bisulphite crystallised on evaporation and consisted chiefly of the dimethyl ketone (VII) which was obtained in large rhombic plates (1 g.) on crystallisation from light petroleum. The monomethyl ketone (II) was converted into the semicarbazone, which, crude, had m. p. 182—184°, raised by one crystallisation from alcohol to 188—190° (Found: C, 63·1; H, 7·0. Calc. for $C_{13}H_{17}O_2N_3$: C, 63·2; H, 6·9%). The m. p. was undepressed by admixture with a specimen prepared as described previously (*loc. cit.*).

It was found that methylation using sodium *iso*propoxide also gave the ketone (II), but here the yield was lower owing to more of the dimethyl ketone being formed.

7-Keto-1-methoxy-13-methyl-5 : 6 : 7 : 9 : 10 : 13-hexahydrophenanthrene (VIII; R = Me).—The diethylaminobutanone methiodide used was prepared according to Wilds (*J. Amer. Chem. Soc.*, 1943, **65**, 471); in our experience it invariably crystallised, provided that the methyl iodide was not added too rapidly.

5-Methoxy-1-methyl-2-tetralone (2·5 g.) was added under nitrogen to a suspension of sodamide (1·05 g.) in benzene (15—20 c.c.). The mixture was shaken in a cold water-bath for 15 minutes. A suspension of diethylaminobutanone methiodide (from 2 g. of the Mannich base) in *iso*propanol (*ca.* 10 c.c.) was added from a hopper. After being shaken in cold water for 15 minute and refluxed gently for a further 15 minutes, the mixture was cooled and treated with dilute sulphuric acid (20 c.c. of 2N). The benzene layer was washed with water and the solvents removed. The residue on distillation gave 2·45 g., nearly all b. p. 160—170°/0·1 mm. The distillate was very viscous, the higher fractions being glassy when cold. The whole was dissolved in ether, concentrated to 6 c.c., and kept at 0° for 2 days. The crystals were washed by decantation with chilled ether and collected (1·6 g.). A small further quantity could be obtained by fractional distillation of the mother liquors. The product so obtained was almost pure; crystallisation from light petroleum (b. p. 40—60°) gave the *methoxy-ketone* in colourless prisms, m. p. 119—120° (Found: C, 79·4; H, 7·2. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%).

The 2 : 4-*dinitrophenylhydrazone* crystallised from dioxan–alcohol in stout, red, four-sided prisms, m. p. 239—242° (decomp.) (Found: N, 13·1. $C_{22}H_{22}O_5N_4$ requires N, 13·3%).

7-Keto-1-methoxy-13-methyl-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydrophenanthrene (IX; R = Me).—The unsaturated ketone (VIII; R = Me) (400 mg.) in alcohol (10 c.c.) was hydrogenated at 15°/1 atm. over platinum oxide (20 mg.). One mol. of hydrogen was absorbed within 20 minutes; hydrogenation then slowed down greatly and was interrupted. After removal of catalyst and solvent the residue was dissolved in hot light petroleum (b. p. 60—80°) and the solution filtered. Next day the product (300 mg.) was collected; it had m. p. 115—117°, sharply depressed by the ketone VIII (R = Me). One crystallisation from ether gave the *ketone* in stout colourless prisms, m. p. 120—121° (Found: C, 78·8; H, 8·5. $C_{16}H_{20}O_2$ requires C, 78·7; H, 8·2%). Unlike the ketone (VIII; R = Me) the molten substance crystallised at once on cooling.

7-Hydroxy-1-methoxy-13-methyl-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydrophenanthrene (X; R = Me).—The ketone (IX; R = Me) (2·5 g.) was hydrogenated at 15°/1 atm. in alcohol (50 c.c.) over platinum oxide (220 mg.). The absorption of hydrogen (one mol.) was complete in an hour. The *product* (2 g.) separated from light petroleum (b. p. 40—60°) in colourless rosettes of fine needles, m. p. 110—112°, softening from 105° (Found: C, 77·6; H, 9·0. $C_{15}H_{22}O_2$ requires C, 78·0; H, 9·0%). The mother liquors were united with a further quantity (0·25 g.) prepared by hydrogenating the mother liquors of the ketone (IX; R = Me), boiled with charcoal, and filtered. On cooling, colourless needles were deposited (0·35 g.), melting sharply at 104—105°. This is apparently one epimer of the *alcohol* (X; R = Me) (Found: C, 77·8; H, 8·8%).

Dehydrogenation of the Alcohol (X; R = Me).—The alcohol (1 g., mixed epimers) was heated with selenium (1·5 g.) at 300—310° for 8 hours. The benzene-soluble fraction was distilled up to 190° (bath temp.)/0·02 mm., and the distillate (0·3 g.) refluxed for an hour with acetic acid (1 c.c.) and hydriodic acid (1 c.c.; *d* 1·7). The phenolic product was separated as usual, crystallised from light petroleum (b. p. 80—100°), sublimed at 115°/0·02 mm., and crystallised again, being obtained as colourless, feathery needles, m. p. 152—153° (Found: C, 86·0; H, 5·1. Calc. for $C_{14}H_{10}O$: C, 85·7; H, 5·5%). Fieser (*J. Amer. Chem. Soc.*, 1929, **51**, 2484) gives m. p. 156° for 1-phenanthrol. A few mg. of an authentic specimen prepared by Professor G. R. Clemo were kindly supplied by the Research Department, Imperial Chemical Industries, Ltd., Dyestuffs Division. This was mixed with an equal quantity of our product and the whole completely sublimed, m. p. 153°. The following reactions were noted with the two specimens. On warming with chloroform, alcohol and a little potassium hydroxide a bluish-green coloration develops; on the addition of water the green colour remains in the chloroform layer. The colour of a sulphuric acid solution is orange-yellow to yellow.

The picrate separated from aqueous-alcoholic solution in red needles, m. p. 178—180° (not recrystallised) (Fieser, *loc. cit.*, m. p. 182° from methanol).

1-Hydroxy-7-keto-13-methyl-5 : 6 : 7 : 9 : 10 : 13-hexahydrophenanthrene (VIII; R = H).—The methoxy-ketone (VIII; R = Me; 1·2 g.) was boiled for ½ hour with acetic acid (18 c.c.) and hydriodic acid (1·8 c.c.; *d* 1·7). The mixture was poured into water containing a little sodium bisulphite and the product extracted with ether. Acetic acid was removed by washing with bicarbonate and the phenol then extracted with 2N-sodium hydroxide which was acidified immediately after separation. The neutral part was treated in the same way with proportionate amounts of acetic and hydriodic acid, and the process was repeated with the neutral fraction surviving the second demethylation. The crystalline phenolic precipitates were united and sublimed at 160—200°/0·1 mm., giving a yellow crystalline powder (810 mg.). A sample was crystallised from toluene before sublimation, then sublimed and washed with benzene, giving the *phenol* (VIII; R = H) in minute crystals, m. p. 208—210° with reddening from 200° (Found: C, 78·5; H, 7·0. $C_{15}H_{16}O_2$

requires C, 78·9; H, 7·0%). The 2 : 4-dinitrophenylhydrazone crystallised from aqueous alcohol in dark red prisms decomposing at about 245°.

1-*Hydroxy*-7-*keto*-13-*methyl*-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-*octahydrophenanthrene* (IX; R = H).—The phenolic ketone (VIII; R = H; 590 mg.) and platinum oxide (30 mg.) were suspended in alcohol (10 c.c.). Hydrogenation at 15°/1 atm. was rapid, one mol. being absorbed in 15 minutes. The reaction was then interrupted and the residue after removal of catalyst and solvent taken up in a little benzene. Next day the crystals (200 mg.) were collected. By shaking the mother liquors in ether with sodium bisulphite solution and decomposition of the resulting insoluble adduct with sodium carbonate, a further quantity (200 mg.) of the same product was obtained. The product sublimed without residue at 160°/0·02 mm. A sample, crystallised from much benzene, gave the *ketone* (IX; R = H) in irregular, colourless prisms, m. p. 190—191° (Found : C, 77·9; H, 7·9. $C_{15}H_{18}O_2$ requires C, 78·2; H, 7·8%). When the phenolic ketone was dissolved in alcohol before hydrogenation, an inferior yield resulted.

1 : 7-*Dihydroxy*-13-*methyl*-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-*octahydrophenanthrene* (X; R = H).—The ketone (IX; R = H) (0·6 g.) in acetic acid (6 c.c.) was hydrogenated at 15°/1 atm. over platinum oxide (40 mg.). One mol. of hydrogen was taken up in an hour. The solvent and catalyst were removed and the residue was taken up in chloroform. Next day the colourless four-sided tabular crystals (0·4 g.) were collected; the *diol* (X; R = H) had m. p. 170—171° (Found : C, 77·2; H, 8·7. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·6%). The same product was obtained by hydrogenating the ketone (VIII; R = H) in acetic acid, or by demethylating the methoxy-alcohol (X; R = Me; mixture of epimers). The diol (X; R = H) crystallised from benzene in large solvated prisms, which melted indefinitely and retained solvent with great tenacity.

1-*Hydroxy*-7-*acetoxy*-13-*methyl*-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-*octahydrophenanthrene* (XI).—The diol (X; R = H; 480 mg.) was boiled for 1 hour with acetic acid (1 c.c.), acetic anhydride (0·24 c.c.), and a few crystals of potassium acetate. On cooling, the product (360 mg.) separated, m. p. 193—194°. Recrystallisation from acetic acid gave the *acetoxy-phenol* (XI) in colourless aggregated prisms, m. p. 196—197° (Found : C, 74·1; H, 7·9. $C_{17}H_{22}O_3$ requires C, 74·4; H, 8·0%). The crystals did not dissolve appreciably in aqueous alkali, but, when an alcoholic solution was precipitated by water, the resulting milky suspension cleared instantly on adding a drop of sodium hydroxide solution.

7-*Hydroxy*-1-*keto*-13-*methyltetradecahydrophenanthrene Semicarbazone*.—The acetoxy-phenol (XI; 360 mg.) with platinum oxide (150 mg.) suspended in acetic acid (3 c.c.) was hydrogenated at ~40°/1 atm. The sparingly soluble phenol gradually dissolved as reduction proceeded. The reduction slackened after the absorption of nearly three mols. of hydrogen (18 hours). Ether was added and the filtered solution washed twice with water and thrice with 5 c.c. portions of 2N-sodium hydroxide. The last two washings gave a slight turbidity on acidification. The ether was removed and the residue (340 mg.; colourless gum) dissolved in acetic acid (8 c.c.) and treated with a solution of chromium trioxide (130 mg.) in acetic acid (2·6 c.c.). After 36 hours water and ether were added, and the ether solution successively washed with water, 2N-alkali, again water, and evaporated. The residue was boiled with alcoholic potash (6 c.c. of N) for 1 hour; the ether-soluble product was then separated from the dark alkaline solution. An attempt to obtain a bisulphite compound proving fruitless, the product was distilled up to 180° (bath temp.)/0·05 mm., the distillate (100 mg.) being taken in two approximately equal fractions. The higher fraction was analysed (Found : C, 77·2; H, 10·4. $C_{15}H_{24}O_2$ requires C, 76·3; H, 10·2%). This indicated that only a slight amount of deoxygenation had taken place. The total distillate was treated with cold aqueous-alcoholic semicarbazide acetate (from 100 mg. of hydrochloride) in the usual manner. Crystallisation set in rapidly. Next day the product (45 mg.) was collected. Recrystallisation from much *iso*butanol gave the *semicarbazone* in small colourless, diamond-shaped prisms, m. p. 244° (decomp.) (Found : C, 65·5; H, 9·3. $C_{16}H_{27}O_2N_3$ requires C, 65·5; H, 9·2%).

1 : 7-*Diketo*-13-*methyltetradecahydrophenanthrene Bis*-2 : 4-*dinitrophenylhydrazone*.—In an early experiment the ketone (VIII; R = H; 180 mg.) with platinum oxide (40 mg.) in acetic acid (3 c.c.) was hydrogenated for 18 hours at ~15°/1 atm. The product was separated into phenolic (110 mg.) and neutral (60 mg.) fractions. From the phenolic part the diol (X; R = H) was isolated. The neutral part was treated with chromium trioxide (52 mg.) in acetic acid (2·6 c.c.). After 36 hours the product, worked up for neutral material as usual, was distilled at 10 mm. and treated with 2 : 4-dinitrophenylhydrazine sulphate in alcohol. Crystallisation first from dioxan and then from dimethylformamide gave yellow, microscopic leaflets, m. p. 255—258° (decomp.) (2 mg.). Analysis was carried out on 1·8 mg. of *substance* (Found : C, 55·2; H, 5·6. $C_{27}H_{30}O_8N_8$ requires C, 54·6; H, 5·1%).

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