139. *Experiments on the Synthesis of Substances related to the Sterols. Part XLIII.*

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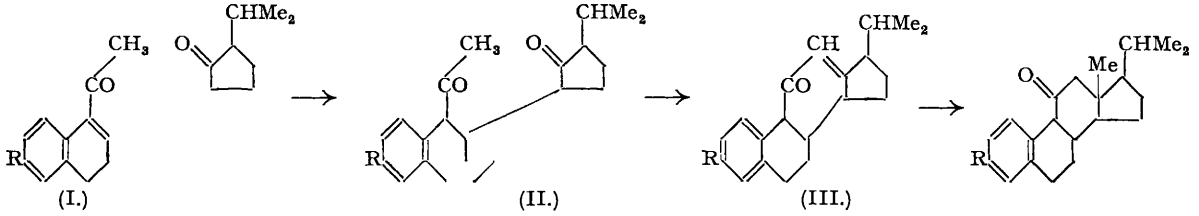
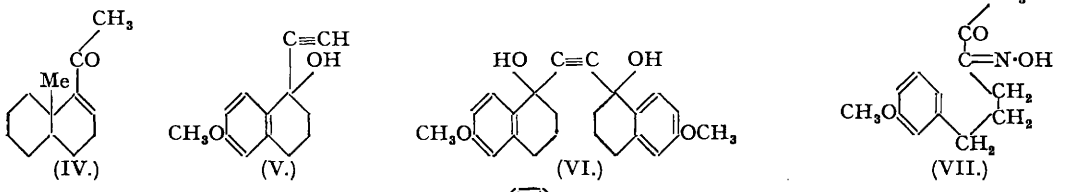
Condensation of (I; R = H, OCH_3) with sodium or lithium 2-*iso*propyl*cyclo*pentanone gives (II; R = H, OCH_3) which may be cyclised by sodium ethoxide, or by heating the sodium or lithium derivative in ether, to (III; R = H, OCH_3), but this does not add methylmagnesium halide to the $\alpha\beta$-double bond in the presence of cuprous halide, the keto-group reacting instead. Compound (IV) is produced by addition of acetylene to 2-keto-9-methyldecalin followed by treatment with mercury acetamide, but fails to add sodium 2-*iso*propyl*cyclo*pentanone.

The construction of the sterol skeleton, ring by ring, must prove very laborious and expensive in materials, so that methods of formation of the complete ring system by locking together two halves are much more attractive. Some progress in this direction has already been made (cf. Peak and Robinson, J., 1937, 1581), but the substances hitherto synthesised lack either angular methyl groups or a substituent at position 17, and introduction of these has proved difficult. The observation (Birch and Robinson, J., 1943, 501) that 2-keto-$\Delta^{1:9}$-octalin can be methylated in the angle group by means of methylmagnesium iodide in the presence of cuprous bromide indicated that the last stage in the type of synthesis outlined below might be possible.

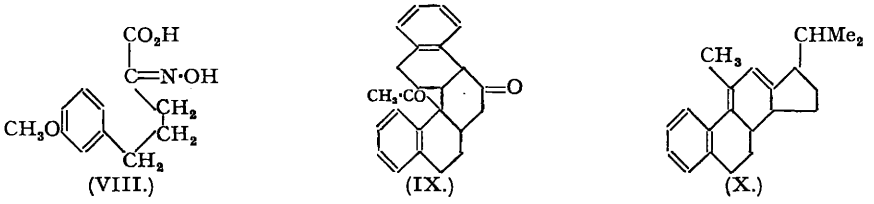


(I.) (II.) (III.)

This, it was hoped, would prove a model for the replacement of (I) by an analogous alicyclic unsaturated ketone which might contain the appropriate angle methyl group and even a second double bond. Further, the side chain of the second component could be that of the sterol, and hence a synthesis of *x*-cholane was envisaged. The preliminary experiments have shown that two of the stages present great difficulty. In the more aromatic series we could not add the angle methyl group and in the alicyclic series we could not bring about the coupling of the two halves. If the latter obstacle could be overcome we do not anticipate trouble with the *C*-methylation in this case.



(IV.) (V.) (VI.) (VII.)



(VIII.) (IX.) (X.)

An attempt was first made to prepare (I; R = OCH_3) from the readily available 1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene. This has been caused to react with acetylenemagnesium bromide (Dane, Höss, Bindseil, and Schmitt, *Annalen*, 1937, **532**, 39) to give 1-hydroxy-6-methoxy-1-ethynyl-1 : 2 : 3 : 4-tetrahydronaphthalene (V), but when this process was repeated on a larger scale, the main product was always the 1 : 4-diol (VI). The ketone did not react at all with sodium or potassium acetylide or hydrogen cyanide. The small amount of (V) obtained could not be converted into (I; R = OCH_3) by formic acid or by the boron trifluoride–ether complex in various solvents, so the method was abandoned.

We next tried to hydrolyse and cyclise (VII) (obtained by the action of nitrous acid on γ-*m*-methoxyphenylpropylacetoacetic acid) by means of acid reagents, but only a small amount of a compound, probably 1-hydroxy-6-methoxy-1-acetyl-1 : 2 : 3 : 4-tetrahydronaphthalene, was obtained. It was found, however, that *2-oximino-5-m-methoxyphenylvaleric acid* (VIII) (obtained by the action of amyl nitrite on sodium ethyl-γ-*m*-methoxyphenylpropylacetoacetate and hydrolysis) cyclised in good yield by the action of a mixture of concentrated hydrochloric and acetic acids on the steam-bath to *6-methoxy-3 : 4-dihydro-1-naphthoic acid*. The acid chloride on treatment with methylzinc iodide gave *6-methoxy-1-acetyl-3 : 4-dihydronaphthalene* (I; R = OCH_3). As a

model, condensations with the more readily available 1-acetyl-3 : 4-dihydronaphthalene (obtained by the action of dimethylzinc on 3 : 4-dihydro-1-naphthoyl chloride) were also investigated.

These acetyl-dihydronaphthalenes added sodium or lithium 2-*iso*propyl*cyclo*pentanone (the latter in better yield) to produce the diketones (II; R = OCH_3, H) which underwent ring-closure to (III; R = OCH_3, H) on treatment with alcoholic sodium ethoxide, or by refluxing the sodium or lithium derivatives in ether. The compound (III; R = H) showed the characteristic αβ-unsaturated ketone absorption band in the ultra-violet, $\lambda_{max.}$, 2410 A.; $\varepsilon_{max.}$, 8080. Direct dehydrogenation by means of palladised charcoal gave a crystalline substance which is probably 4-*hydroxy*-3'-iso*propyl*-1 : 2-cyclo*pentenophenanthrene* but reduction by means of sodium in alcohol, followed by treatment with selenium at 320°, gave 3'-*iso*propyl-1 : 2-*cyclo*pentenophenanthrene, the ultra-violet absorption spectrum of which closely resembled that of 1 : 2-*cyclo*pentenophenanthrene itself. The properties of the substance agree with the description by Riegel, Gold, and Kubico (*J. Amer. Chem. Soc.*, 1943, **65**, 1772) who have synthesised it since this work was completed. Similarly, reduction of (III; R = OCH_3) followed by selenium dehydrogenation gave 7-*methoxy*-3'-iso*propyl*-1 : 2-cyclo*pentenophenanthrene*. The retention of the *iso*propyl group in these dehydrogenation products proves that addition of the 2-*iso*propyl*cyclo*pentanone has not taken place in the alternative position to give an angular *iso*propyl group on C_1, since this would be eliminated in the dehydrogenation.

In addition to the 4-*keto*-3'-iso*propyl*-1 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-cyclo*pentenophenanthrene* (III; R = H), a second substance was isolated from the condensations with (I; R = H) which was evidently the *dimer* of the latter, and by analogy with the results of Jones and Koch (J., 1942, 393) may be formulated as (IX).

By the action of methylmagnesium iodide or bromide in the presence of cuprous bromide or chloride, (III; R = H) gave only a small amount of material extractable by the Girard–Sandulesco reagent P, and this was shown by its ultra-violet absorption spectrum and preparation of the 2 : 4-dinitrophenylhydrazone to be mainly unchanged (III; R = H). It may have been converted by the Grignard reagent into the enol magnesium halide. The main product of the reaction was (X). The compound (III; R = OCH_3) gave no ketonic material extractable by the Girard–Sandulesco reagent P.

In an attempt to arrive at the fully saturated sterol skeleton, the preparation and condensations of (IV) were investigated. 1-Keto-9-methyldecalin reacted readily with sodium acetylide in liquid ammonia to give 1-*hydroxy*-9-*methyl*-1-*ethynyldecalin*, and this gave (IV) by the action of mercury acetamide (cf. Aeschbacher and Goldberg, *Helv. Chim. Acta*, 1939, **22**, 1185; Goldberg, Aeschbacher, and Hardegger, *ibid.*, 1943, **26**, 680). The unsaturated ketone did not react with sodium 2-*iso*propyl*cyclo*pentanone. The investigation will be continued.

Experimental.

Ethyl γ-m-*Methoxyphenylpropylacetoacetate.*—γ-*m*-Methoxyphenylpropyl iodide (Schlittler and Robinson, J., 1935, 1288) (100 g.) was added to a solution of sodium (12·5 g.) and ethyl acetoacetate (71 g.) in alcohol (150 c.c.). After refluxing for 6 hours, the product was worked up in the usual manner and obtained as a colourless oil (75 g.), b. p. 155—157°/0·2 mm. (Found: C, 69·2; H, 8·4. $C_{16}H_{22}O_4$ requires C, 69·1; H, 8·0%).

3-*Oximino*-2-*keto*-6-m-*methoxyphenylhexane.*—(A) The above ester (10 g.) was refluxed with 4% sodium hydroxide solution (150 c.c.) for 6 hours. 2-Keto-6-*m*-methoxyphenylhexane was obtained as a colourless oil, b. p. 180°/14 mm. Its 2 : 4-dinitrophenylhydrazone crystallised from benzene–alcohol in orange prisms, m. p. 94°. The *semicarbazone* crystallised from alcohol as colourless prisms, m. p. 114° (Found: C, 63·7; H, 7·7. $C_{14}H_{21}O_2N_3$ requires C, 63·8; H, 7·9%). Concentrated hydrochloric acid (4 c.c.) was slowly added to a mixture of the ketone (9 g.) and amyl nitrite (5 g.), cooled in ice. Extraction of the product with an excess of dilute aqueous sodium hydroxide gave a yellow solution, which deposited a yellow oil on acidification. Kept in the refrigerator in contact with light petroleum, this deposited crystals, which recrystallised from light petroleum (b. p. 80—100°) as pearly plates (2·5 g.), m. p. 62°, identical with the substance obtained below.

(B) The above ester (10 g.) was shaken with 2% sodium hydroxide solution (150 c.c.) for 24 hours, most of it then having dissolved. A little oil was removed by ether, and sodium nitrite (2·5 g.) added to the ice-cold solution, which was then acidified. After 8 hours the product was extracted with ether, the ether removed, and the residue extracted with successive portions of boiling light petroleum (b. p. 60—80°) until only a little tar was left. The product crystallised from the solution as colourless, pearly plates (4·5 g.), m. p. 62° (Found: C, 66·5; H, 7·5. $C_{13}H_{17}O_3N$ requires C, 66·4; H, 7·2%).

Attempts to hydrolyse and cyclise this substance to (I; R = OCH_3) with 65% sulphuric acid or a mixture of equal volumes of concentrated hydrochloric and acetic acids on the steam-bath, gave tars. By the latter process a small amount of an oil, b. p. 130°/0·1 mm., was obtained, which gave a dark red 2 : 4-*dinitrophenylhydrazone* (prisms from benzene), m. p. 233° (Found: C, 57·2; H, 4·7. $C_{19}H_{20}O_8N_4$ requires C, 57·0; H, 5·0%). This may be a derivative of 1-hydroxy-6-methoxy-1-acetyl-1 : 2 : 3 : 4-tetrahydronaphthalene.

2-*Oximino*-5-m-*methoxyphenylvaleric Acid.*—Ethyl γ-*m*-methoxyphenylpropylacetoacetate (70 g.) was added to sodium (7 g.) in alcohol (100 c.c.), and the mixture cooled in ice. Amyl nitrite (30 g.) was added in 15 minutes with shaking, the mixture left in cold water for an hour, and then refluxed for 10 minutes. Aqueous sodium hydroxide (200 c.c. of 20%) was added, and refluxing continued for an hour. The mixture was then poured into water (200 c.c.), and the cold solution extracted twice with ether (100 c.c.). It was acidified with dilute sulphuric acid, the oil taken up in ether, and the extract shaken with successive portions of potassium bicarbonate solution until no more acidic material was extracted. Acidification gave a cream-coloured solid (45 g.), a little of which recrystallised from benzene–light petroleum as colourless needles, m. p. 119° (Found: C, 61·0; H, 6·25. $C_{13}H_{15}O_4N$ requires C, 60·7; H, 6·3%).

6-*Methoxy*-3 : 4-*dihydro*-1-*naphthoic Acid.*—The above crude acid (45 g.) was heated on the steam-bath with a mixture of concentrated hydrochloric acid (75 c.c.) and acetic acid (75 c.c.). It passed into solution and crystals began to appear after 15 minutes. After a further 15 minutes the solution was cooled, and water (30 c.c.) added. The solid was crystallised from aqueous acetic acid and obtained as large colourless prisms (31 g.), m. p. 130—131° (Found: C, 70·3; H, 6·0. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%). A little more was recovered by dilution of the mother-liquor. Catalytic reduction of the acid (1 g.) in sodium carbonate solution in the presence of Raney nickel proceeded rapidly, hydrogen (120 c.c.) being absorbed (Calc. for one double bond: 110 c.c.).

The 6-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthoic acid* crystallised from ethyl acetate–petroleum (b. p. 60—80°) as colourless flat prisms, m. p. 89° (Found : C, 69·9; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·8; H, 6·8%).

6-*Methoxy*-1-*acetyl*-3 : 4-*dihydronaphthalene* (I; R = OCH_3).—Phosphorus trichloride (2·5 g.) was added to the above dihydro-acid (7·5 g.) in benzene (150 c.c.), the mixture kept for 2 hours, and then heated to 65° for 90 minutes. The benzene layer was decanted, and the solvent removed under reduced pressure. The product was not distilled, since an attempt to do so at 0·1 mm. resulted in partial decomposition. A small portion treated with aqueous ammonia gave the amide, m. p. 191° (needles from methyl alcohol). The acid chloride (8 g.) in benzene (45 c.c.) was added with stirring and ice-cooling to a solution of methylzinc iodide, prepared from zinc–copper couple and methyl iodide (15 g.), and ethyl acetate (3 g.) in toluene (30 c.c.). After 15 minutes at the room temperature, the mixture was decomposed with ice and dilute hydrochloric acid, and the organic layer refluxed with dilute sodium hydroxide (100 c.c., 10%) for 30 minutes to remove a little ester. The product was obtained as a very pale yellow, viscous oil (4·4 g.), b. p. 200°/16 mm. (Found : C, 76·5; H, 7·2. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%). The *semicarbazone* crystallised from methyl alcohol as colourless prisms, m. p. 120° (Found : C, 64·7; H, 6·8. $C_{14}H_{17}O_2N_3$ requires C, 64·7; H, 6·75%).

1-*Acetyl*-3 : 4-*dihydronaphthalene* (I; R = H).—3 : 4-Dihydro-1-naphthoic acid (28 g.) (Sowinski, *Ber.*, 1891, **24**, 1357) and thionyl chloride (45 c.c.) were refluxed for 20 minutes, excess thionyl chloride removed under reduced pressure and 3 : 4-dihydro-1-naphthoyl chloride distilled as a colourless, pungent oil (28 g.), b. p. 174°/14 mm. A small amount treated with aqueous ammonia gave the amide, m. p. 128° (colourless needles from methyl alcohol). The acid chloride (28 g.) was dissolved in benzene (100 c.c.), cooled in ice, and stirred under nitrogen, and dimethylzinc (7 g.) in benzene (40 c.c.) added during 15 minutes. After a further 15 minutes at room temperature the mixture was decomposed with ice and dilute hydrochloric acid, the benzene removed, and the residue refluxed with 10% sodium hydroxide solution for 15 minutes to remove a little ester. Longer heating with alkali resulted in the formation of notable quantities of the dimer, m. p. 215°, described below. The product was obtained as a colourless, pleasant-smelling oil (17 g.), b. p. 165°/11 mm. (Found : C, 83·6; H, 6·9. $C_{12}H_{12}O$ requires C, 83·7; H, 6·9%). The *semicarbazone* crystallised from methyl alcohol in colourless needles, m. p. 208° (Found : C, 68·75; H, 6·4. $C_{13}H_{15}ON_3$ requires C, 68·2; H, 6·55%), and the 2 : 4-dinitrophenylhydrazone separated from benzene–alcohol in orange-red prisms, m. p. 119—120°.

The ketone (1 g.) was heated with sulphur (0·15 g.) to 220—230° for 2 hours, giving an oil; picrate, m.p. 116°, semicarbazone, m. p. 232°, both undepressed by mixture with the corresponding derivatives of 1-acetylnaphthalene.

Condensation of 1-*Acetyl*-3 : 4-*dihydronaphthalene with* 2-iso*Propyl*cyclo*pentanone*.—(A) 2-*iso*Propyl*cyclo*pentanone (6·5 g.) and powdered sodamide (2·5 g.) were refluxed in ether (40 c.c.) for 7 hours in a current of nitrogen. 1-Acetyl-3 : 4-dihydronaphthalene (10 g.) in ether (30 c.c.) was then slowly added with stirring and ice-cooling. After 12 hours at room temperature, the mixture was refluxed for 30 minutes and then decomposed with ice. After evaporation of a part of the ether, crystals separated and were removed. Extraction of the solid with boiling alcohol left white crystals (3 g.), m. p. 215° (Found : C, 83·3; H, 7·1. $C_{24}H_{24}O_2$ requires C, 83·7; H, 6·9%). The substance was evidently a *dimer* of the acetyl-dihydronaphthalene, probably (IX).

Concentration of the alcoholic extract gave another substance which separated from benzene–light petroleum as white needles (2·5 g.), m. p. 126° (Found : C, 80·5; H, 8·7. $C_{20}H_{26}O_3$ requires C, 80·5; H, 9·0%). The ultra-violet absorption spectrum in alcohol showed a benzene-type band with maxima at 2660 A. and 2645 A., log $\varepsilon_{max.}$, 2·65, and the substance is therefore probably the diketone (II; R = H). It was heated with sodium (0·1 g.) in alcohol (3 c.c.) in an atmosphere of nitrogen on the steam-bath for an hour. The product was a glass, b. p. 193—195°/0·08 mm. (Found : C, 84·3; H, 8·4. $C_{20}H_{24}O$ requires C, 85·7; H, 8·6%). It had probably cyclised, in the main, to (III; R = H). The ethereal solution from the original condensation also gave the same substance on distillation (4 g.), b. p. 198—200°/0·1 mm. (Found : C, 85·2; H, 8·2%).

(B) Lithium (0·7 g.) was converted into the amide by the catalytic action of a trace of ferric nitrate on its solution in liquid ammonia (25 c.c.), the ammonia removed, and dry ether (75 c.c.) added. 2-*iso*Propyl*cyclo*pentanone (12·6 g.) was added with stirring under nitrogen, and the solution refluxed for an hour. 1-Acetyl-3 : 4-dihydronaphthalene (17·2 g.) was then added with stirring and ice-cooling over 15 minutes, the mixture left for 1 hour, and refluxed for 3½ hours. Worked up as above, the crystalline dimer (2·5 g.) was obtained together with (III; R = H) as a glass (16·8 g.), b. p. 193—198°/0·1 mm. (Found : C, 85·4; H, 8·3%). The ultra-violet absorption spectrum showed the typical $\alpha\beta$-unsaturated ketone band at 2410 A.; $\varepsilon_{max.}$, 8080, agreeing fairly closely with the value of 2390 A. given by Woodward (*J. Amer. Chem. Soc.*, 1941, **63**, 1123) for the absorption maximum of a $\beta\beta$-dialkyl $\alpha\beta$-unsaturated ketone. The 2 : 4-*dinitrophenylhydrazone* was obtained as a dark red, amorphous solid, which could not be obtained crystalline, being probably a mixture of *cis*- and *trans*-isomers, but which was purified by passage through a column of alumina in benzene–light petroleum solution. It melted indefinitely at about 85—87° (Found : C, 68·1; H, 6·1; N, 12·7. $C_{26}H_{28}O_4N_4$ requires C, 67·8; H, 6·0; N, 12·2%).

Direct dehydrogenation of the ketone (1 g.) by means of palladised charcoal at 260° for 2 hours gave a solid (0·4 g.) which crystallised from benzene–light petroleum as colourless prisms, m. p. 162° (sintered 158°) (Found : C, 86·8; H, 7·4. $C_{20}H_{20}O$ requires C, 86·9; H, 7·2%). This is probably 4-*hydroxy*-3′-iso*propyl*-1 : 2-cyclo*pentenophenanthrene*, although it was not soluble in dilute aqueous sodium hydroxide. The picrate was obtained as orange needles, m. p. 148—152°.

Reduction of the ketone (1·0 g.) with sodium (5 g.) in alcohol (50 c.c.) and heating the product with selenium (2 g.) to 320° for 5 hours gave an oxygen-free product. This was isolated (crude, m. p. 93°; 450 mg.) by extraction with boiling alcohol, and after several recrystallisations from alcohol, 3′-*iso*propyl-1 : 2-*cyclo*pentenophenanthrene was obtained as colourless plates, m. p. 96° (Found : C, 92·0; H, 7·6. Calc. for $C_{20}H_{20}$: C, 92·3; H, 7·7%). Riegel, Gold, and Kubico (*loc. cit.*) give m. p. 97·6—98·4°. The *picrate* crystallised from alcoholic picric acid as bright yellow needles, m. p. 121° (Found : N, 8·9. $C_{26}H_{23}O_7N_3$ requires N, 8·9%). The 1 : 3 : 5-trinitrobenzene derivative consisted of pale yellow prisms, from alcohol, m. p. 115°.

The ultra-violet absorption spectrum resembled that of 1 : 2-*cyclo*pentenophenanthrene itself, given by Mayneord and Roe (*Proc. Roy. Soc.*, 1935, **152** A, 317). The maxima are compared in the table below, *A* being 3′-*iso*propyl-1 : 2-*cyclo*pentenophenanthrene and *B* 1 : 2-*cyclo*pentenophenanthrene. The main bands are in italics.

A. $\lambda_{max.}$	*3515*	3440	*3355*	3290	*3205*	*3005*	*2890*	*2820*	*2605*		
log $\varepsilon_{max.}$	2·98	2·52	2·88	2·58	2·76	4·06	3·98	3·98	4·74		
B. $\lambda_{max.}$	*3520*	3440	*3360*	3290	*3210*	3140	*3005*	*2880*	*2800*	*2570*	*2150*
log $\varepsilon_{max.}$	2·99	2·55	2·99	2·54	2·74	2·55	4·22	4·10	4·16	4·80	4·50

Condensations of 6-*Methoxy*-1-*acetyl*-3 : 4-*dihydronaphthalene and* 2-iso*Propyl*cyclo*pentanone*.—2-*iso*Propyl*cyclo*pentanone (2·8 g.) and lithium amide (from lithium, 0·18 g.) were refluxed in dry ether (15 c.c.) for 1½ hours, the solution cooled in ice, and 6-methoxy-1-acetyl-3 : 4-dihydronaphthalene (4·4 g.) in ether (15 c.c.) slowly added with stirring under nitrogen. After refluxing for 3 hours, dry alcohol (15 c.c.) was added, and refluxing continued for 1 hour. Addition of dilute hydrochloric acid, extraction with ether and distillation gave the product as a glass (3·8 g.), b. p. 220—

235°/0·1 mm. Redistillation gave a pale yellow glass (3·1 g.), b. p. 128—134°/0·15 mm. (Found: C, 80·3; H, 8·2. $C_{21}H_{26}O_2$ requires C, 81·3; H, 8·4%). That this was mainly 4-*keto*-7-*methoxy*-3′-iso*propyl*-1 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-cyclo*pentenophenanthrene* was shown by dehydrogenation. The substance (1 g.) was reduced with sodium (1 g.) and alcohol (10 c.c.), and the product heated with selenium (2 g.) to 320—330° for 5 hours. Extraction with boiling alcohol gave the product as pearly plates (230 mg.). It was purified by passage through alumina in benzene solution, and crystallised from alcohol as colourless plates, m.p. 129° (Found: C, 86·0; H, 7·5. $C_{21}H_{22}O$ requires C, 86·8; H, 7·6%). Alcoholic picric acid gave the picrate as bright orange needles, m. p. 156°.

The ketone gave no crystalline derivative with semicarbazide or 2 : 4-dinitrophenylhydrazine.

If the refluxing in the original condensation was omitted, a considerable proportion of a crystalline solid was obtained. This crystallised from alcohol as colourless needles, m. p. 171—173° (Found: C, 76·6; H, 8·7. $C_{21}H_{28}O_3$ requires C, 76·8; H, 8·6%). It was therefore 6-*methoxy*-2-(3′-iso*propyl*cyclo*pentan*-2′-*onyl*)-1-*acetyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (II; R = OCH_3).

Reactions with Grignard Reagents.—Keto*iso*propylhexahydro*cyclo*pentenophenanthrene (2 g.) in dry ether (20 c.c.) was added slowly with stirring and cooling under nitrogen to a Grignard solution from magnesium (0·2 g.) and methyl iodide (1 g.) in ether (10 c.c.) with addition of cuprous bromide (0·05 g.). A further 0·05 g. was added half-way through the mixing. After decomposition in the usual manner, the product was separated by the Girard–Sandulesco reagent P into a ketonic and a non-ketonic fraction. The latter was heated to 180° with a trace of iodine, a little water being evolved. Distillation gave a colourless oil (1·4 g.), b. p. 190°/0·1 mm. (Found: C, 90·3; H, 9·7. $C_{21}H_{26}$ requires C, 90·6; H, 9·4%). It was, therefore, 4-*methyl*-3-iso*propyl*-1 : 9 : 10 : 11-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene* (X). The ketonic fraction distilled as a glass (0·3 g.), b. p. 190—195°/0·1 mm. (Found: C, 85·1; H, 9·0. $C_{20}H_{24}O$ requires C, 85·7; H, 8·6%. $C_{21}H_{28}O$ requires C, 85·1; H, 9·5%). The ultra-violet absorption spectrum still showed the $\alpha\beta$-unsaturated ketone band at 2390 A., although $\varepsilon_{max.}$ was lower at about 5000. It gave a 2 : 4-dinitrophenylhydrazone as a red amorphous solid, m. p. *ca.* 85° (Found: C, 67·4; H, 6·3. Calc. for $C_{26}H_{28}O_4N_4$: C, 67·8; H, 6·0%). It therefore corresponded to starting material, from the 2 : 4-dinitrophenylhydrazone of which it could not be separated by chromatographing in benzene–light petroleum on alumina.

The analysis and the low value of $\varepsilon_{max.}$ probably indicate the presence of a little of the desired product.

Repetition of the Grignard addition under varying conditions, using methylmagnesium bromide and cuprous chloride, gave essentially the same results. In the case of ketomethoxy*iso*propylhexahydro*cyclo*pentenophenanthrene the Grignard additions did not give any ketonic substance extractable by the Girard–Sandulesco reagent P.

The following experiments were made in collaboration with Mr. G. F. Beattie.

1-*Hydroxy*-9-*methyl*-1-*ethynyldecalin.*—A mixture of *cis*- and *trans*-1-keto-9-methyldecalin (8·3 g.) (obtained by the method of Birch and Robinson) (cf. preceding paper) in ether (15 c.c.) was slowly added to a liquid ammonia solution of sodium acetylide, from sodium (1·3 g.) in liquid ammonia (50 c.c.), in a 150 c.c. Dewar flask. Acetylene was bubbled through the mixture for 3 hours and it was then left for 12 hours. After decomposition with ice the product was taken up in ether, dried and distilled. It was a colourless, camphoraceous oil (8 g.), b. p. 130—132°/9 mm. (Found: C, 81·1; H, 10·8. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%).

1-*Acetyl*-9-*methyl*-Δ^1-*octalin.*—Attempts to produce this substance from the above ethynylcarbinol by the action of formic acid or boron trifluoride–ether in acetic acid or alcohol did not give the required product. It was obtained as follows. The ethynylcarbinol (19 g.) and mercury acetamide (58 g.) were refluxed in absolute alcohol (140 c.c.) for 3 hours. After saturation with hydrogen sulphide, the mercuric sulphide was coagulated by the addition of a few drops of concentrated hydrochloric acid and removed by centrifuging. Distillation gave a colourless oil (11 g.), b. p. 110—140°/9 mm. This was warmed on the steam-bath with an excess of aqueous-alcoholic semicarbazide acetate for 15 minutes, giving a colourless semicarbazone, m. p. 200—205°, undepressed by the semicarbazone of the original 1-keto-9-methyldecalin. On refluxing with 10% hydrochloric acid it gave this ketone as a colourless, camphoraceous oil (4 g.), b. p. 110—112°/9 mm. The mother-liquor from the semicarbazide was diluted with water, extracted with ether and distilled, giving fractions, b. p. 120—128°/9 mm. (2 g.), 135—137°/9 mm. (4 g.). The latter fraction was the required substance (Found: C, 81·3; H, 10·9. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%). It showed the $\alpha\beta$-dialkyl $\alpha\beta$-unsaturated ketone band in the ultra-violet at $\lambda_{max.}$ 2370 A.; $\varepsilon_{max.}$ 7690. On treatment with 2 : 4-dinitrophenylhydrazine sulphate in alcohol it gave a solid 2 : 4-*dinitrophenylhydrazone* in 93% yield, crystallising as bright orange prisms from benzene–alcohol, m. p. 143—146° (Found: C, 60·9; H, 6·5. $C_{19}H_{24}O_4N_4$ requires C, 61·3; H, 6·5%). A sample of the pure cis-2 : 4-*dinitrophenylhydrazone*, prepared in the same manner from *cis*-1-keto-9-methyldecalin made by the method of Elliott and Linstead (J., 1938, 662), had m. p. 169° (Found: C, 60·9; H, 6·4. $C_{19}H_{24}O_4N_4$ requires C, 61·3; H, 6·5%).

The ketone failed to condense with sodium 2-*iso*propyl*cyclo*pentanone in ether or boiling benzene.

Absorption spectra are by Dr. F. B. Strauss.

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