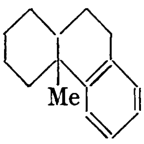
258. *Syntheses of Polycyclic Compounds Related to the Sterols. Part I.*

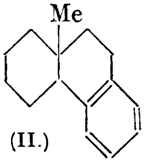
By G. A. R. Kon.

The object of the present series of investigations is the synthetic preparation of polycyclic structures related to the sterols and polyterpenes. Our knowledge of this important group is based almost wholly on the study of degradation products, but the time is now ripe for supplementing this by synthesis.

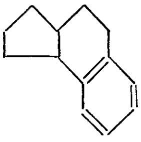
As a preliminary step it was proposed to study the formation of hydrocarbons possessing an appropriate skeleton, especially those consisting of a five-membered ring combined with a naphthalene or phenanthrene residue, and to examine the possibility of introducing methyl groups in the positions assigned to them in the sterol formulæ current at the moment; with this object in view the following have been prepared:

(I.)



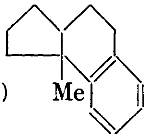


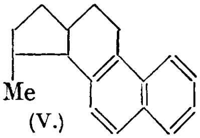
(II.)



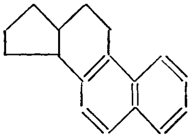
(III.)

(IV.)





(V.)

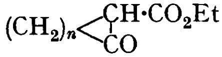


(VI.)

The preparation of other compounds is in progress, but in view of the publication of a paper by Cook and Hewett (*Chem. and Ind.*, 1933, **52**, 451; see this vol., p. 1098) it was thought desirable to publish the results obtained without delay, having regard to their bearing on the problem of the structure of " Diels's hydrocarbon " $C_{18}H_{16}$ (or $C_{17}H_{14}$).

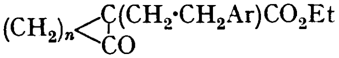
The elucidation of the structure of this hydrocarbon was one of the objects of this work, and for this purpose the dehydrogenation of the hydrocarbons (I)—(VI) has been carried out.

For the preparation of the compounds themselves, the phenanthrene synthesis of Bardhan and Sengupta (J., 1932, 2520) by the cyclisation of α-phenylethyl*cyclo*hexanols has been extended and adapted. In the first place, it was found that *cyclo*pentanols could be used just as readily as *cyclo*hexanols, the compounds (III)—(VI) being obtained in this way; and the α-naphthyl grouping could be introduced in place of phenyl (*compounds* V and VI). The hydrolysis of the esters of the type (VIII) to the ketones constituted the principal obstacle, as the method originally used gives a poor yield and sometimes fails altogether (Bardhan and Sengupta, *ibid.*, p. 2798). It has now been found that the esters can be hydrolysed to the corresponding adipic or pimelic acids (IX) and that these undergo cyclisation with ease :



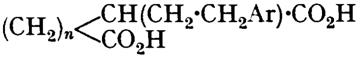
$(CH_2)_n<\begin{array}{l}CH\cdot CO_2Et\\ CO\end{array}$

(VII.)



$(CH_2)_n<\begin{array}{l}C(CH_2\cdot CH_2Ar)CO_2Et\\ CO\end{array}$

(VIII.)

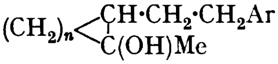


$(CH_2)_n<\begin{array}{l}CH(CH_2\cdot CH_2Ar)\cdot CO_2H\\ CO_2H\end{array}$

(IX.)

$(CH_2)_n<\begin{array}{l}CH\cdot CH_2\cdot CH_2Ar\\ CO\end{array}$

(X.)



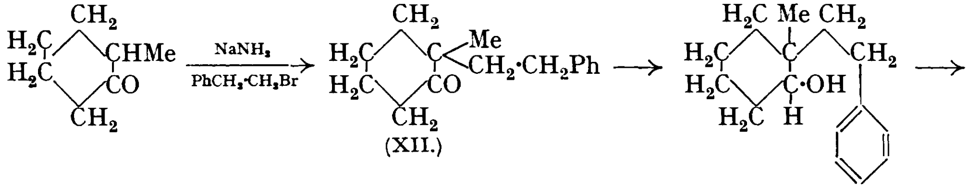
$(CH_2)_n<\begin{array}{l}CH\cdot CH_2\cdot CH_2Ar\\ C(OH)Me\end{array}$

(XI.)

(Ar = Ph or α-$C_{10}H_7$; n = 3 or 4.)

The ketones are then reduced to the secondary alcohols and dehydrated.

For the introduction of the methyl group on a carbon atom common to two rings, the ketones are converted into the tertiary alcohols (XI), which undergo ring closure just like the secondary alcohols, giving the *compounds* (I) and (IV). To obtain the alternative structure (II), advantage was taken of the observations of Haller and Cornubert (*Bull. Soc. chim.*, 1927, **41**, 367) on the alkylation of α-substituted cyclic ketones with sodamide. The second alkyl group enters almost entirely in the α, not the α′, position; in this way the introduction of the phenylethyl group into 2-methyl*cyclo*hexanone should yield the ketone (XII), which on reduction and cyclisation should pass into the hydrocarbon (II), as was indeed the case; the ketone (XII) can also be prepared by the methylation of α-phenylethyl*cyclo*hexanone and the same reaction can doubtless be applied to the corresponding *cyclo*pentanones. The structure of the ketone (XII) follows from the fact that the hydrocarbon (II) gives phenanthrene, and not methylphenanthrene, on dehydrogenation.

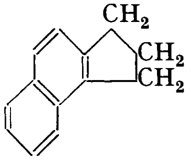


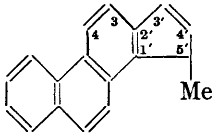
(XII.) (II.)

The reduction of the naphthylated ketones to the corresponding *cyclo*pentanols is abnormal, inasmuch as two additional atoms of hydrogen appear to be taken up; the resulting hydrocarbons also appear to be the dihydro-derivatives of (V) and (VI) respectively. Other methods of reduction are now under investigation.

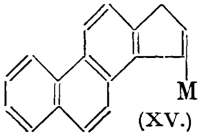
The dehydrogenation of the compounds (I)—(VI) is of considerable interest. It may be stated at once that whilst the dehydrogenation of (I) and (II) readily gives phenanthrene in good yield, that of the *cyclo*pentane compounds proceeds much less smoothly, especially with the two simplest. Both (III) and (IV) yield, as the only isolable product, the same liquid 4 : 5-*benzohydrindene* (XIII), although this is doubtless only one of the products in a complex reaction. The compound (V), on the other hand, yielded exclusively the corresponding indene, 1 : 2-$\Delta^{1':3'}$(or $\Delta^{1':4'}$)-5′-*methyl*cyclo*pentadienophenanthrene* (XIV or XV) :

(XIII.)





(XIV.)

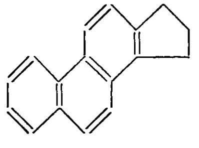


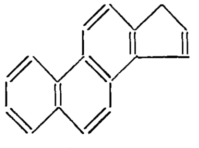
(XV.)

Now, the compound (V) was originally prepared because it was expected to give on dehydrogenation the dihydro-derivative of (XIV), which would be identical with Diels's hydrocarbon if the latter has the structure considered probable by Ruzicka and Thomann (*Helv. Chim. Acta*, 1933, **16**, 216); it has not yet been possible to effect the reduction of (XIV) to the hydrindene, and the work has been postponed in view of recent developments.

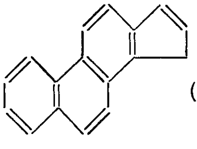
The compound (VI) gave on dehydrogenation a product very similar at first sight to the indene (XIV or XV), but it soon became apparent that it could not be a pure compound, although its high m. p. appeared to preclude the presence of a hydrindene. Ultimately, a separation was effected by means of the picrates; that of 1 : 2-cyclo*pentenophenanthrene* (XVI), although present in relatively small amount, is the less soluble and can be recognised by its beautiful crystalline form; it melts at 133—134° and the pure hydrocarbon regenerated from it at 135—136°.

(XVI.)





or



(XVII.)

These compounds therefore appear to be identical with the *cyclo*pentenophenanthrene and its picrate, the preparation of which has been announced by Cook and Hewett (*loc. cit.*).* A comparison of the new hydrocarbon has been made with a specimen of Diels's hydrocarbon, m. p. 126—128°, for the loan of which the author is greatly indebted to Dr. O. Rosenheim. An approximately equimolecular mixture of the two melts at 130—132°, and a mixture of the picrates also shows an intermediate m. p. There is therefore a considerable probability that Diels's hydrocarbon is somewhat impure *cyclo*pentenophenanthrene; it is hoped to make a more exhaustive comparison of the two in the near future. It must, however, be borne in mind that Jacobs and Fleck (*J. Biol. Chem.*, 1932, **97**, 57) have found that the m. p. of Diels's hydrocarbon is not depressed by the admixture of a possible dimethylphenanthrene isolated by them from strophanthidin, although they succeeded in demonstrating that the two compounds were not identical. Clearly, therefore, the greatest caution is necessary in this case, especially when it is remembered that the compounds (XVI) and (XVII) also form mixtures of intermediate m. p.

Note.—Since the above was written, Ruzicka, Ehmann, Goldberg, and Hösli (*Helv. Chim. Acta*, 1933, **16**, 833) have described the synthesis of *cyclo*pentenophenanthrene and two of its methyl derivatives; the properties of the former agree perfectly with those given in the present paper and their theoretical conclusions are essentially the same.

EXPERIMENTAL.

Ethyl 1-β-*Phenylethyl*cyclo*hexan-2-one-*1-*carboxylate* (with Z. T. LING).—This was prepared as described by Bardhan and Sengupta (*loc. cit.*); the yield is improved (65%) by carrying out the reaction in xylene solution at the b. p. of the latter (paraffin-bath).

α-(β-*Phenylethyl*)*pimelic acid* (IX; $n = 4$, Ar = Ph). The above ester was boiled with twice its weight of baryta in 4 volumes of water over-night; the cooled solution was strongly acidified with hydrochloric acid, and the precipitated oil taken up in ether. The new *acid* could be separated from the small amount of 1-β-phenylethyl*cyclo*hexanone formed by shaking with aqueous sodium carbonate and reprecipitation; it solidified after some weeks, forming rosettes of crystals, m. p. 64—65°, but it could not be satisfactorily recrystallised (Found : C, 67·9; H, 8·0. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·7%). For the preparation of the ketone this separation is unnecessary; the ethereal extract is roughly dried, evaporated, and the residue slowly distilled at atmospheric pressure from an air-bath. The distillate is taken up in ether, washed with alkali, dried, and evaporated, the residue being distilled, giving a 70% yield of the ketone, which can be purified through the semicarbazone with very little loss.

The same ketone was also obtained, though in very poor yield, by the action of phenylethyl bromide on the sodio-derivative of *cyclo*hexanone (see p. 1084); it was identified by its semicarbazone, m. p. 179—180° (Bardhan and Sengupta, *loc. cit.*) (Found : C, 69·3; H, 8·3. Calc. : C, 69·5; H, 8·1%).

1-*Methyl*-2-β-*phenylethyl*cyclo*hexanol* (XI; $n = 4$, Ar = Ph). 50 G. of the ketone regenerated

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* Dr. J. W. Cook has informed the author that his pure hydrocarbon melts at 135° and not 153° as originally stated (see this vol., p. 1109).

from the semicarbazone were slowly added to an excess of methylmagnesium iodide cooled in ice; after standing over-night the mixture was warmed for 0·5 hour, decomposed with ice and dilute acetic acid, and the product isolated by means of ether, 36 g. of crude alcohol being obtained. This was freed from unchanged ketone by shaking for 0·5 hour with semicarbazide acetate solution, 7 g. of semicarbazone being recovered. The *alcohol* boiled at 140°/3 mm. as a slightly viscous oil with a lemon-like odour (Found : C, 82·7; H, 9·9. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%).

12-*Methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* (I).—The dehydration of the alcohol with phosphoric oxide was carried out as described by Bardhan and Sengupta (*loc. cit.*). The *hydrocarbon* was twice boiled with sodium and had b. p. 157°/16 mm., $d_{4°}^{18·2°}$ 1·0082, n_D 1·55437, $[R_L]_D$ 63·66 (Calc., 63·47, on the basis of Auwers's value for tetralin). It was stable to alkaline permanganate and did not decolorise bromine in chloroform (Found : C, 89·5; H, 9 8. $C_{15}H_{20}$ requires C, 89·9; H, 10·1%).

Dehydrogenation. The hydrocarbon was heated with twice its weight of selenium to 260° for 2 hours and to 320—340° for 20 hours. A part of the product sublimed into the condenser, whilst the rest was recovered by extraction with ether, and solidified on removal of the solvent. It was converted into the picrate, which was identified as phenanthrene picrate (m. p. and mixed m. p. 144—145°), and from which the hydrocarbon was recovered by boiling with ammonia; it had m. p. and mixed m. p. 99—100° after crystallisation from acetic acid (charcoal) (Found : C, 94·3; H, 5·7. Calc. : C, 94·4; H, 5·7%).

2-*Methyl*-2-β-*phenylethyl*cyclo*hexanone* (XII).—A suspension of 20 g. of finely powdered sodamide in 300 c.c. of benzene was warmed in a three-necked flask provided with a condenser and stirrer, whilst 56 g. of 2-methyl*cyclo*hexanone were slowly run in, the stirring being continued until no more ammonia was evolved (2—3 hours). A slight excess of β-phenylethyl bromide was then added, and the mixture boiled over-night. After addition of water, the washed and dried benzene solution was distilled under reduced pressure with a column. Most of the starting material was recovered unchanged, but some 15 g. of a fraction, b. p. *ca.* 152°/4 mm., were obtained and converted into the *semicarbazone*. This formed somewhat indefinite nodules after two crystallisations from methyl alcohol, m. p. 178° (sharp), unaltered on further crystallisation (Found : C, 70·2; H, 8·8. $C_{16}H_{21}ON_3$ requires C, 70·3; H, 8·5%). The ketone regenerated from it had b. p. 150°/2·8 mm.,* $d_{4°}^{19·0°}$ 1·0085, n_D 1·51042.

2-*Methyl*-2-β-*phenylethyl*cyclo*hexanol* (with W. E. BATTEN). The ketone was reduced as described by Bardhan and Sengupta (*loc. cit.*), giving a 90% yield of the *alcohol*, b. p. 159°/3·0 mm. (Found : C, 82·4; H, 10·4. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%).

11-*Methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* (II).—The dehydration of the alcohol and the purification of the *hydrocarbon* were carried out as before; the product, obtained in very good yield, had b. p. 133°/2·8 mm., $d_{4°}^{18·5°}$ 1·0054, n_D 1·55254, $[R_L]_D$ 63·66 (calc., 63·47); it was stable to permanganate and did not decolorise bromine (Found : C, 89·7; H, 10·0. $C_{15}H_{20}$ requires C, 89·9; H, 10·1%).

Dehydrogenation. This proceeded exactly as with the 12-methyl compound and gave a good yield of phenanthrene, identified as before.

Ethyl 2-β-*Phenylethyl*cyclo*pentan*-1-*one*-2-*carboxylate* (VIII; $n = 3$, Ar = Ph) (with Z. T. LING).—Ethyl *cyclo*pentanonecarboxylate gave a 70% yield of the phenylethyl derivative even in benzene solution; the crude *ester* boiled at 180—195°/6 mm., mainly at 192°/6 mm. on re-distillation (Found : C, 73·7; H, 8·0. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·8%). The *semicarbazone* crystallised from methyl alcohol in plates, m. p. 163° (Found : C, 64·2; H, 7·1; N, 13·7. $C_{17}H_{23}O_3N_3$ requires C, 64·4; H, 7·2; N, 13·3%).

α-(β-*Phenylethyl*)*adipic acid* (IX; $n = 3$, Ar = Ph). Hydrolysis of the above ester with 10% aqueous potash (Bardhan and Sengupta, *loc. cit.*) was tedious and gave a very poor yield of ketone (20%); boiling with 10% sulphuric acid was even less successful. The method described on p. 1083 was then adopted; only a small amount of ketone was obtained, and an 85—90% yield of the *acid*, m. p. 97—98° after repeated crystallisation from dilute alcohol and finally from benzene–petroleum (Found : C, 67·0; H, 7·4. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%); the acid showed little tendency to crystallise.

2-β-*Phenylethyl*cyclo*pentanone* (X; $n = 3$, Ar = Ph). This ketone was formed in small amount as described above, also in over 80% yield by the cyclisation of the acid (p. 1083); yields of 70% of ketone are readily obtained from the crude ketonic ester. The ketone purified by distillation boiled at 146°/6 mm. and was sufficiently pure for all purposes; a specimen re-

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* The accurate pressures recorded were read with a Leybold vacuoscope.

generated from the *semicarbazone*, which formed very sparingly soluble plates from methyl alcohol, m. p. 213° (decomp.) (Found : C, 68·7; H, 7·9; N, 17·4. $C_{14}H_{19}ON_3$ requires C, 68·6; H, 7·8; N, 17·1%), had b. p. 163°/13 mm., $d_{4^\circ}^{16\cdot5^\circ}$ 1·0026, n_D 1·52840.

1-*Methyl*-2-β-*phenylethyl*cyclo*pentanol* (XI; *n* = 3, Ar = Ph). The ketone was treated with methylmagnesium iodide, and the product purified as described on p. 1084, giving an 80% yield of the *alcohol*, b. p. 134—135°/5 mm. (Found : C, 82·4; H, 9·7. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%), a little ketone being recovered as semicarbazone. The alcohol possesses a rose-like odour and is very readily dehydrated on heating. The product is an unsaturated *hydrocarbon* which is rapidly attacked by permanganate and instantly decolorises bromine in chloroform; after repeated boiling with sodium, it had b. p. 120°/7 mm., $d_{4^\circ}^{17\cdot0^\circ}$ 0·93701, n_D 1·52662, $[R_L]_D$ 61·11 (calc., for $|^{=}_{4}$, 61·07) (Found : C, 90·2; H, 9·6. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%).

1 : 2-cyclo*Pentano*-1-*methyl*-1 : 2 : 3 : 4 : *tetrahydronaphthalene* (IV).—On dehydrating the alcohol with phosphoric oxide, a saturated *hydrocarbon* was obtained; after the usual purification it had b. p. 128°/12 mm., $d_{4^\circ}^{17\cdot8^\circ}$ 0·99798, n_D 1·54790, $[R_L]_D$ 59·23 (calc., 59·11). Some specimens contained small amounts of the unsaturated isomeride, as shown by a higher molecular refraction and a reaction with bromine and permanganate; the pure hydrocarbon (IV) is, however, definitely less stable to these reagents than either (I) or (II) (Found : C, 90·0; H, 9·7. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%).

Dehydrogenation. In contrast to the compounds (I) and (II), the dehydrogenation of (IV) proceeds with some difficulty. The hydrocarbon was kept vigorously boiling with twice its weight of selenium for 24 hours, after which the temperature rose slowly to 360° and remained constant for 18 hours. The black pitch produced was very intractable; attempts to distil it led to much decomposition, only a few drops of a yellow liquid containing much red selenium being obtained. The liquid was taken up in ether, repeatedly filtered, evaporated, and the residue converted into the *picrate*, orange needles, m. p. 108°, which could not be recrystallised and gave only approximate figures on analysis (Found : C, 55·9; H, 5·8. $C_{19}H_{15}O_7N_3$ requires C, 57·7; H, 3·7%). The *hydrocarbon* recovered by boiling with ammonia was evidently the pure 4 : 5-benzohydrindene (XIII), b. p. 118°/0·5 mm., $d_{4^\circ}^{19\cdot6^\circ}$ 1·0569, n_D 1·62649, $[R_L]_D$ 56·35 (Found : C, 92·4; H, 7·3. $C_{13}H_{12}$ requires C, 92·8; H, 7·2%).

In other experiments, the original black product was extracted with ether in a Soxhlet extractor for some days, an intensely fluorescent solution being obtained. This gave on evaporation an oil containing a sparingly soluble red solid; the only product obtained on distillation was the above hydrocarbon.

2-β-*Phenylethyl*cyclo*pentanol* (with W. E. Batten).—The ketone was reduced as described by Bardhan and Sengupta (*loc. cit.*), giving an 85% yield of the *alcohol*, b. p. 131°/1·5 mm.; the reduction was complete, as the product did not react with semicarbazide (Found : C, 81·3; H, 9·4. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%). Attempts to effect reduction as described by Nenitzescu and Ionescu (*Bull. Soc. chim. Romania*, 1933, **14**, 65) were unsuccessful, most of the ketone being recovered unchanged.

1 : 2-cyclo*Pentano*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (III).—The *hydrocarbon* obtained by the dehydration of the above alcohol boiled after purification at 138°/19 mm., $d_{4^\circ}^{19\cdot4^\circ}$ 1·0054, n_D 1·55297, $[R_L]_D$ 54·78 (calc., 54·49) (Found : C, 90·3; H, 9·4. $C_{13}H_{16}$ requires C, 90·7; H, 9·3%).

Dehydrogenation. This was carried out in the same way and with the same result as with the 1-methyl compound (above), but the yield of the hydrocarbon (XIII) was better. After regeneration from the picrate (m. p. and mixed m. p. 108°), it boiled at 146°/6 mm., $d_{4^\circ}^{17\cdot5^\circ}$ 1·0679, n_D 1·63328, $[R_L]_D$ 56·25 (Found : C, 92·8; H, 7·3. Calc.: C, 92·8; H, 7·2%).

β-(α-*Naphthyl*)*ethyl Bromide*.—β-(α-Naphthyl)ethyl alcohol, prepared from α-bromonaphthalene and ethylene chlorohydrin, phenylmagnesium bromide being used to block the hydroxyl group of the latter (Grignard, *Compt. rend.*, 1905, **141**, 44), was converted into the bromide by heating with 5 volumes of 30% hydrobromic acid in acetic acid in a soda-water bottle to 100° for 14—16 hours; the product (73% yield) isolated by means of ether boiled at 172°/20 mm.

Ethyl 5-*Methyl*cyclo*pentanone*-2-*carboxylate* (with E. C. H. Lawrence).—This ester was prepared from ethyl adipate essentially as described by Cornubert and Borrel (*Bull. Soc. chim.*, 1930, **47**, 304), except that the methylation of ethyl *cyclo*pentanonecarboxylate was carried out with the aid of molecular sodium in benzene; the alternative method using sodium ethoxide is uncertain in spite of all precautions.

Ethyl 5-*methyl*-2-β-(α-*naphthyl*)*ethyl*cyclo*pentanone*-2-*carboxylate* (as VIII; *n* = 3, Ar = α-$C_{10}H_7$). Attempts to condense the potassio-derivative of the above ester with naphthylethyl bromide in benzene solution gave a very poor yield of the desired high fraction. The condensation was therefore conducted in xylene solution at the b. p. of the latter for 40 hours. The product gave on fractionation a 65% yield of a dark amber-coloured oil, b. p. 190—240°/3 mm.; the pure ester boils at about 227°/4 mm.

α-Methyl-α'-[β-(α-naphthyl)ethyl]adipic acid. The above crude ester was hydrolysed without further purification; hydrolysis with baryta was slow and incomplete, but it was readily achieved by adding the ester to twice its weight of potassium hydroxide in 3 volumes of water with enough alcohol to give a clear solution and boiling gently, the alcohol being allowed to distil off through a column; the last traces were removed in a vacuum, the mixture diluted, and worked up as described on p. 1083. A little crude ketone was obtained and some 70% of the *acid*, small prisms, m. p. 155—156° after two crystallisations from dilute alcohol and one from acetone–benzene (Found: C, 72·2; H, 6·8. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·0%).

*5-Methyl-2-β-(α-naphthyl)ethyl*cyclo*pentanone.* The acid was slowly distilled under a pressure of 100—200 mm. until only a small carbonaceous residue remained in the flask, and the *ketone* isolated as before, a yield of 70% being obtained, b. p. 222—225°/10 mm., 188—190°/3 mm. This was sufficiently pure for subsequent operations (Found: C, 85·3; H, 7·9. $C_{18}H_{20}O$ requires C, 85·7; H, 7·9%). The *semicarbazone* formed with some difficulty and was first obtained as a sticky solid; it was rubbed with ether and formed thick crystals from methyl alcohol, m. p. 171—172° (Found: C, 73·4; H, 7·5. $C_{19}H_{23}ON_3$ requires C, 73·8; H, 7·4%).

*5-Methyl-2-β-(α-naphthyl)ethyl*cyclo*pentanol*(?). The reduction of the ketone (27·5 g.) gave 22 g. of the *alcohol*, b. p. 177°/4·5 mm.; the b. p. is somewhat uncertain owing to the extreme viscosity of the compound (Found: C, 84·3, 84·3; H, 9·0, 9·1. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%. $C_{18}H_{24}O$ requires C, 84·3; H, 9·4%).

1 : 2-(*5'-Methyl*cyclo*pentano*)-1 : 2 : 3 : *4-tetrahydrophenanthrene*(?) (V).—The alcohol was heated to 200° with twice its weight of phosphoric oxide for 30 minutes under reduced pressure. The mass was cooled in ice, and a little ice cautiously added with shaking, then sufficient ice-water to dissolve the solid; the *hydrocarbon* was extracted with ether, the extract washed with alkali, dried, and evaporated, the crude hydrocarbon being purified by boiling with sodium. It then boiled at 141—145°/2 mm. and had $d_{4°}^{18\cdot9°}$ 1·0302, n_D 1·57307, and was stable to permanganate and bromine (Found: C, 91·0; H, 9·2. $C_{18}H_{22}$ requires C, 90·8; H, 9·2%).

Dehydrogenation. This was carried out as before (p. 1085); the product on distillation gave a yellow oil with a green fluorescence, which rapidly solidified; the solid on crystallisation from petroleum (b. p. 40—60°) gave fine plates, m. p. 182°, consisting of the *indene* (XIV or XV) and a careful search failed to reveal the presence of the corresponding hydrindene even in traces (Found: C, 93·8, 93·8; H, 6·3, 6·3. $C_{18}H_{12}$ requires C, 93·9; H, 6·1%). The *picrate* formed characteristic dark red needles from benzene–petroleum, m. p. 199—200° (decomp.); it could not be recrystallised from alcohol owing to partial dissociation (Found: C, 62·6; H, 3·6. $C_{24}H_{17}O_7N_3$ requires C, 62·7; H, 3·7%).

The reduction of the hydrocarbon with sodium in 95% alcohol, although causing a fall in the m. p., did not yield a pure product; other methods of reduction are under investigation.

*Ethyl 2-β-(α-Naphthylethyl)*cyclo*pentanone-2-carboxylate* (VIII; $n = 3$, Ar = α-$C_{10}H_7$).—This ester was obtained from ethyl *cyclo*pentanonecarboxylate exactly as described on p. 1085, the yield of crude ester, b. p. 210—235°/2 mm., being 65%; a little high-boiling fraction was also collected, and found to consist mainly of the same ester.

α-[β-(α-Naphthyl)ethyl]adipic acid (IX; $n = 3$, Ar = α-$C_{10}H_7$). The hydrolysis of the ester with potassium hydroxide (above) gave but little ketone and a good yield of the *acid*, m. p. 152—153° after two crystallisations from dilute alcohol and one from acetone–benzene–petroleum (Found: C, 72·0; H, 7·0. $C_{18}H_{20}O_4$ requires C, 72·0; H, 6·7%).

*2-β-(α-Naphthylethyl)*cyclo*pentanone* (X; $n = 3$, Ar = α-$C_{10}H_7$). This ketone, obtained in 45% yield by the pyrolysis of the above acid as described above, boiled at 178°/2 mm. The *semicarbazone* formed readily but was somewhat caseous, forming spherical nodules from methyl alcohol, m. p. 192—193° (Found: C, 72·8; H, 7·1. $C_{18}H_{21}ON_3$ requires C, 73·2; H, 7·1%).

*2-β-(α-Naphthyl)ethyl*cyclo*pentanol*(?). The reduction of the ketone gave an extremely viscous, colourless oil, b. p. *ca.* 180°/2·2 mm., in about 80% yield; the reduction was complete, as no trace of semicarbazone could be obtained from the *product* (Found: C, 84·3; H, 8·9. $C_{17}H_{22}O$ requires C, 84·3; H, 9·1%).

1 : 2-cyclo*Pentano*-1 : 2 : 3 : *4-tetrahydrophenanthrene*(?) (VI).—The alcohol was dehydrated as described above and gave a moderate yield of the *hydrocarbon*, which after purification had b. p. 142°/2 mm., $d_{4°}^{19\cdot6°}$ 1·0336, n_D 1·57446, and was a colourless oil with a fine violet fluorescence; it was stable to permanganate and to bromine in chloroform (Found: C, 90·8; H, 9·0. $C_{17}H_{18}$ requires C, 91·1; H, 8·9%).

Dehydrogenation. This proceeded in the same way as that of the higher homologue, but there was very little decomposition on distillation, and the yield of hydrocarbon was consequently better. After one crystallisation, this had m. p. 169—170°, rising to about 180° on further crystallisation, but analysis showed that it was a mixture (Found : C, 93·7, 93·8, 93·7; H, 6·2, 6·0, 6·0. $C_{17}H_{12}$ requires C, 94·4; H, 5·6. $C_{17}H_{14}$ requires C, 93·6; H, 6·4%). It was therefore converted into the picrate in benzene solution; the latter on cooling deposited two kinds of crystals, which were roughly separated by hand. One variety, which appeared to be the less soluble though present in smaller quantity, formed fine long orange needles, m. p. 133—134° after repeated crystallisation from benzene–petroleum; great care is required in recrystallising this compound as it tends to decompose. This proved to be the *picrate* of 1 : 2-cyclo*pentenophenanthrene* (XVI) (Found: C, 61·4, 61·4, 61·9; H, 4·0, 4·1, 4·0. $C_{23}H_{17}O_7N_3$ requires C, 61·7; H, 3·8%). The *hydrocarbon* regenerated from the picrate with ammonia was pure, because both the crystals obtained by recrystallisation from petroleum and those from the mother-liquor melted sharply at 135—136°; the compound crystallises particularly well from light petroleum (Found: C, 93·5, 93·4; H, 6·5, 6·5%). The *trinitrobenzene* derivative formed yellow needles from methyl alcohol, m. p. 165·5° (Found : C, 64·0; H, 4·1. $C_{23}H_{17}O_6N_3$ requires C, 64·0; H, 4·0%). The picrate remaining after the removal of the picrate of m. p. 133—134° was recrystallised several times from benzene, but its crystalline form remained indefinite and the m. p. about 124°. The hydrocarbon was regenerated from it and formed fine plates from acetone m. p. 182—183°, consisting of 1 : 2-$\Delta^{1':3'}$(or $\Delta^{1':4'}$)-cyclo*pentadienophenanthrene* (XVII) (Found : C, 94·5; H, 5·8. $C_{17}H_{12}$ requires C, 94·4; H, 5·6%). A mixture of equal amounts of (XVI) and (XVII) melted at about 155°.

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