88. *The Synthesis of Compounds related to the Sterols, Bile Acids, and Oestrus-producing Hormones. Part II. The Formation of some Tetracyclic Hydroaromatic Hydrocarbons.*

By J. W. Cook and C. L. Hewett.

THE mild conditions which suffice for the ring closure of 1-(β-1'-naphthylethyl)-Δ¹-*cyclo*-pentene (I) (J., 1933, 1098) appear to preclude molecular rearrangement, in which case the number of saturated isomerides which might be formed is confined to the four compounds represented by structures (II) to (V). By the simple and convenient method

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

(IV.)   (V.)
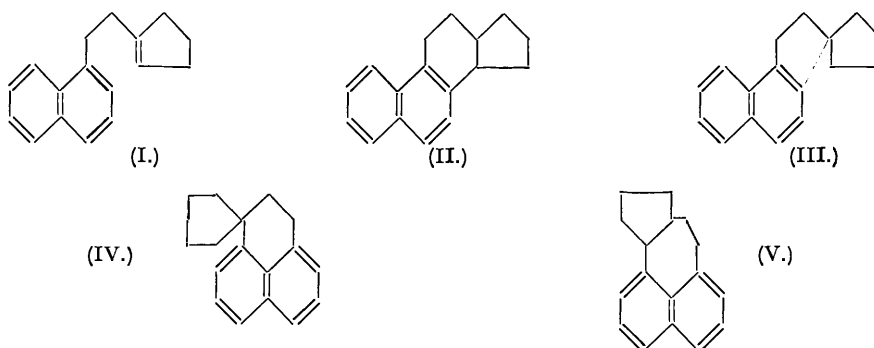
(*loc. cit.*) for the preparation of 1 : 2-*cyclo*pentenophenanthrene (arising from the dehydrogenation of II), under all the conditions which were used for ring closure, a considerable proportion of (I) was converted into a hydrocarbon, $C_{17}H_{18}$, which was regarded as the *trans*-isomeride of (II), although it was pointed out that structure (IV) was not excluded. We have now shown that this hydrocarbon cannot be represented by (II), for oxidation with dilute nitric acid led to a nitrobenzenetricarboxylic acid. A di- or a tetra-carboxylic acid might arise from (II), but not a tricarboxylic acid. Our oxidation product, which we isolated as its *methyl* ester, was shown to be 4-nitrohemimellitic acid, for the same ester was obtained when 4-nitronaphthalic acid was oxidised under similar conditions. Further evidence against formula (II) was provided by the fact that cyclisation of 1-(β-1'-*naphthylethyl*)-Δ¹-cyclo*hexene, obtained by dehydration of the *carbinol* formed by the interaction of *cyclo*hexanone with β-1'-naphthylethylmagnesium chloride,* led to a mixture of tetracyclic hydrocarbons from which were isolated not only the two stereoisomeric as-*octahydrochrysenes* (VI), but also an isomeric *hydrocarbon* ($C_{18}H_{20}$) which in its physical properties

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* This is a process analogous to the formation of 1-β-phenylethyl*cyclo*hexanol and 1-β-phenylethyl-Δ¹-*cyclo*hexene, which, together with 1-phenylacetyl-Δ¹-*cyclo*hexene, we described in Part I. These three compounds have also been prepared by Fulton and Robinson (J., 1933, 1463).

and in the bright vermilion colour of its sparingly soluble *picrate* was exactly analogous to the hydrocarbon $C_{17}H_{18}$ under discussion. This analogy is exemplified by the following table :

	M. p. of hydrocarbon.	M. p. of picrate.	*d.*	n_D.	$[R_L]_D$.
$C_{17}H_{18}$	35°	128°	1·0859	1·6256	0·3240
$C_{18}H_{20}$	55	141	1·0809	1·6197	0·3248

The hydrocarbon $C_{18}H_{20}$ gave no chrysene when heated with selenium and hence could not be an octahydrochrysene (VI), a fact which renders it unlikely that the hydrocarbon $C_{17}H_{18}$ has the structure (II), analogous to (VI).

It thus remained to distinguish between formulæ (IV) and (V) for the hydrocarbon $C_{17}H_{18}$. On general grounds (V) is unlikely. It is true that von Braun and Rath (*Ber.*, 1927, **60**, 1182) synthesised a somewhat analogous ring system with a five-membered ring fused to a seven-membered ring, but they obtained very poor yields and in their case no alternative mode of ring closure was possible. Moreover, a considerable proportion of our tetracyclic hydrocarbon $C_{18}H_{20}$ was recovered unchanged after heating with selenium at 320—340° for 33 hours. It is difficult to reconcile this with a structure analogous to (V), and we therefore conclude that our two hydrocarbons are represented by (IV) and (VII) respectively. Their products of dehydrogenation are consistent with this view, for Clemo and Ormston (*J.*, 1933, 352) showed that spirans undergo rearrangement when heated with selenium, *cyclo*hexyl*spirocyclo*pentane being converted into naphthalene. From the dehydrogenation of the hydrocarbon $C_{18}H_{20}$ (VII) we isolated pyrene (VIII), so ring fission in the position indicated by the dotted line is followed by formation of the pyrene ring system with loss of two carbon atoms.


(VI.)   (VII.)   (VIII.)
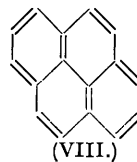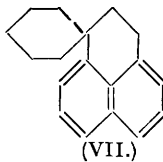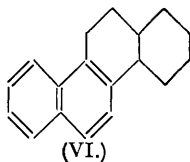
In our previous communication we showed that selenium dehydrogenation of the hydrocarbon $C_{17}H_{18}$ (IV) leads to a hydrocarbon $C_{17}H_{12}$, which we then regarded as an indene corresponding to (II). In its properties (characteristic series of colour and fluorescence changes with concentrated sulphuric acid ; dark red, very sparingly soluble picrate ; unsaturation towards pyridine sulphate dibromide) this hydrocarbon closely resembles pyrene, and it is clearly 1-*methylpyrene* formed by rearrangement of the five-membered ring of (IV). Ample confirmation of this view is provided by comparison of the absorption curve of this hydrocarbon with the characteristic curve of pyrene ; each of the twelve absorption bands of pyrene is reproduced by the hydrocarbon $C_{17}H_{12}$, with a shift towards the region of longer wave-length due to the methyl group. The absorption maxima (Å.) of the two compounds are as follows :

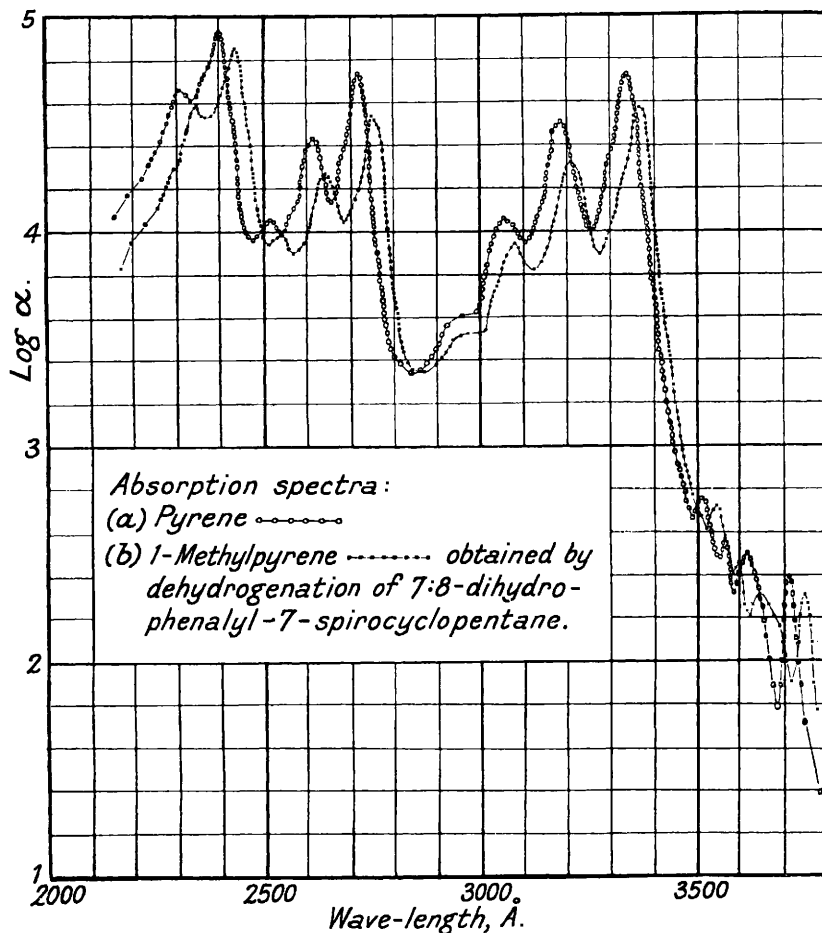|												
Pyrene	3710	3612	3560	3510	3343	3188	3060	2725	2616	2517	2401	2310
1-Methylpyrene	3743	3640	3589	3538	3363	3208	3079	2750	2643	2537	2434	2344

With a view to obtain additional confirmation of our conclusion we attempted to synthesise 1-methylpyrene by an independent method, but although we were able to devise a new synthetic method for pyrene itself we failed to extend it to 1-methylpyrene.

For the synthesis of pyrene, 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene was submitted to the Reformatsky reaction with ethyl bromoacetate. The resulting *acid* (probably IX) was dehydrated to a *ketone* (probably X), which passed into pyrene on reduction and subsequent dehydrogenation. Since compounds related to 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene are now readily available (Haworth, *J.*, 1932, 1125, 1784, 2717), this method of pyrene-ring synthesis will be a useful supplement to the four existing methods (Weitzenböck, *Monatsh.*, 1913, **34**, 193 ; Freund and Fleischer, *Annalen*, 1914, **402**, 77 ; Fleischer and Retze, *Ber.*, 1922, **55**, 3280 ; von Braun and Rath, *Ber.*, 1928, **61**, 956). The failure

of the 1-methylpyrene synthesis was due to the fact that 4-keto-3-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene would not condense with ethyl bromoacetate.
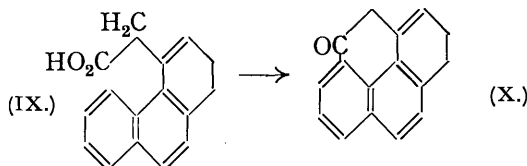
When 1 : 2-*cyclo*pentenophenanthrene was obtained by selenium dehydrogenation of (II) it was always contaminated with a substance which raised its m. p. by varying amounts

Absorption spectra:
(a) Pyrene ∘—∘—∘—∘
(b) 1-Methylpyrene ‑‑‑‑‑‑‑ obtained by dehydrogenation of 7:8-dihydrophenalyl-7-spirocyclopentane.

Log α.

Wave-length, Å.

(Cook and Hewett, *loc. cit.*). This substance was isolated in a pure state by Kon (J., 1933, 1087), who used a method essentially the same as ours in principle although much less direct. Kon showed that the contaminating substance was a hydrocarbon, $C_{17}H_{12}$, and he attributed to it the structure of an indene corresponding to (II). We noticed that the m. p.'s recorded by Kon for the hydrocarbon and its picrate were in good agreement with those of chrysofluorene ($C_{17}H_{12}$; XV) and its picrate, and we found that a sample of chrysofluorene synthesised by a method described in the sequel did not depress the m. p. of the hydrocarbon * isolated from crude 1 : 2-*cyclo*pentenophenanthrene and also

* Dr. G. A. R. Kon very kindly supplied us with a pure specimen of this hydrocarbon. Our identification of the hydrocarbon as chrysofluorene has been confirmed by the oxidation of a larger sample, also supplied by Dr. Kon, to " chrysene ketone."

raised the m. p. of 1 : 2-*cyclo*pentenophenanthrene. Chrysofluorene (XV) could clearly arise by rearrangement of the spiran (III) during selenium dehydrogenation, and we regard these experiments as demonstrating the presence of this spiran in the crude mixture of tetracyclic hydrocarbons obtained from (I). As a corollary it follows that there is now no evidence that dehydrogenation of a five-membered ring can occur under the influence of selenium, for the only remaining example which suggests such a dehydrogenation is the 5′-methyl-1 : 2-*cyclo*pentadienophenanthrene of Kon (*loc. cit.*) and it now seems clear that this substance must be a dimethylpyrene (probably 1 : 2-) formed from a spiran analogous to (IV) by a rearrangement of the type already discussed. The behaviour of polycyclic compounds containing a five-membered ring thus conforms to that of the mono-cyclic *cyclo*pentane derivatives which Zelinsky, Michlina, and Eventowa (*Ber.*, 1933, **66,** 1422) showed to be resistant to the action of a dehydrogenating catalyst.

The separation of the two stereoisomeric *as*-octahydrochrysenes (VI) isolated from the mixture of tetracyclic hydrocarbons formed from 1-(β-1′-naphthylethyl)-Δ¹-*cyclo*-hexene is a matter of considerable difficulty, and is unnecessary if the object is the synthesis of chrysene, for which purpose a convenient method is selenium treatment at 300—320° of the mixture of hydrocarbons formed from 1-(β-1′-naphthylethyl)*cyclo*hexanol by the action of sulphuric acid in acetic acid at 100°. The spiran (VII) is unaffected under these conditions and is readily removed from the sparingly soluble chrysene.

The structure assigned to the two *as*-octahydrochrysenes is based on the fact that they are both smoothly dehydrogenated to chrysene by selenium at 300—310°. Chrysene might, of course, arise from a spiran analogous to (III), but we consider that such a structure is precluded for our two hydrocarbons by the facility with which chrysene was formed, for the spirans which we have investigated require appreciably higher temperatures for rearrangement. Both hydrocarbons differ in their properties from the *s*-octahydrochrysene described by von Braun and Irmisch (*Ber.*, 1932, **65,** 883), and their behaviour towards picric acid is noteworthy. The higher-melting (probably *trans*-) isomeride gave no picrate in methyl-alcoholic solution, whereas the lower-melting (probably *cis*-) compound gave a well-defined orange *picrate* containing two molecules of hydrocarbon combined with one molecule of picric acid. This is very unusual, the only other example we know being the picrate of *s*-octahydroanthracene described by Godchot (*Bull. Soc. chim.*, 1904, **31,** 1340 ; *Ann. Chim.*, 1907, **12,** 484), the existence of which was subsequently denied by Schroeter (*Ber.*, 1924, **57,** 2007). Dr. A. Girard, of Paris, has informed us that some of the oestrus-producing hormones which he has isolated from the urine of pregnant mares give " semi-picrates " of this nature.

In order to examine the possibility of synthesising the spirans (IV) and (VII) we at-tempted to prepare the " dihydrophenalone " (XI) which Mayer and Sieglitz (*Ber.*, 1922, **55,** 1844) obtained by the action of aluminium chloride on β-1-naphthylpropionyl chloride. We have been unable to reproduce their results, for although we obtained a crude product having approximately the m. p. (85—86°) which they record, repeated crystallisation led to the isolation of the yellow 9-phenalone (XII),* m. p. 153—154°, evidently formed by dehydrogenation of the dihydro-compound (XI) first formed.

(XI.)   (XII.)   (XIII.)
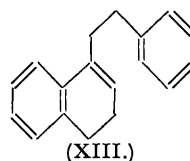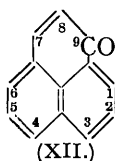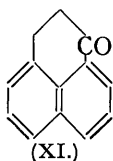
* Three different systems of terminology have been proposed for compounds containing this ring system. For the parent aromatic hydrocarbon corresponding to (XII) the following names have been suggested :

(i) *peri*-Naphthindene (Stelzner, *Lit.-Reg. der Organ. Chem.*, 1914—15, Vol. III, p. 61). This system is used by Criegee, Kraft, and Rank (*Annalen*, 1933, **507,** 177) for a methyl derivative of our ketone.

(ii) Phenalene (= phenonaphthalene) (Mayer and Sieglitz, *loc. cit.*, p. 1837).

(iii) Benznaphthene (= *peri*-benzonaphthalene) (von Braun and Rath, *Ber.*, 1928, **61,** 960).

None of these names is strictly correct, but in order to avoid adding to the confusion we refrain

9-Phenalone has marked basic properties and dissolves immediately in concentrated hydrochloric acid, by which it may be extracted from the crude reaction products and thus readily obtained pure. The same ketone was formed in moderately good yield by treatment of β-1-naphthylpropionic acid with anhydrous stannic chloride. A by-product of this reaction was a colourless ketone, m. p. 120°, either the true 7 : 8-dihydro-9-phenalone (XI) or the isomeric 4 : 5-benz-1-hydrindone. With the small amount of material available we have been unable to determine which of these alternatives is correct.

In the patent literature (D.R.-P. 283,066) is described the synthesis from α- or β-naphthol and glycerol of a compound to which formula (XII) is correctly attributed, for its properties agree in every detail with those of our 9-phenalone. The same formula (XII) should also represent the " pyrene ketone " obtained by Bamberger and Philip (*Annalen*, 1887, **240**, 178) by degradation of pyrene. Apart from its low m. p. (142°), the properties of " pyrene ketone " correspond to those of 9-phenalone.

Ring closure of compounds of type (I) would be expected to lead to *trans*-locking of the rings, and in the hope of obtaining evidence on this point an attempt was made to prepare a hexahydrochrysene by cyclisation of 1-β-*phenylethyl*-3 : 4-*dihydronaphthalene* (XIII), obtained by dehydration of the crude carbinol resulting from 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene and β-phenylethylmagnesium chloride. Both *cis-* and *trans*-hexahydrochrysenes are crystalline solids of known configuration (Ramage and Robinson, J., 1933, 607). When the dialin (XIII) was treated with aluminium chloride in carbon disulphide at 0° the expected cyclisation did not occur, almost the sole reaction being dehydrogenation to 1-β-*phenylethylnaphthalene*.* This facile dehydrogenation of a dihydroaromatic structure imposes a limitation on the utility of the cyclisation reaction as a synthetic method. We propose to attempt to overcome this difficulty by the use of α-decalone instead of α-tetralone, although here an additional complication is introduced by the fact that α-decalols tend to dehydrate largely to the $\Delta^{1:9}$-octalins rather than the $\Delta^{1:2}$-compounds (Hückel and Naab, *Annalen*, 1933, **502**, 139).

For identification of the 1-β-phenylethylnaphthalene formed from (XIII) a specimen was prepared by the Clemmensen reduction of 1-*phenylacetylnaphthalene*. The formation of this ketone (m. p. 57°) from naphthalene and phenylacetyl chloride was claimed by Graebe and Bungener (*Ber.*, 1879, **12**, 1078), and we had no difficulty in preparing by this reaction a highly crystalline substance, m. p. 55—58°. This, however, was shown to be a mixture containing at least 20% of the 2-isomeride. By fractional crystallisation of the *picrates* the mixture was readily separated, and the pure 1-phenylacetylnaphthalene (m. p. 66—67°) was isolated. These experiments show that the conclusion of one of us (Cook, J., 1931, 2012) that 1-phenylacetylnaphthalene is converted into the 2-isomeride by heat was unjustified, for the earlier experiment was made with the material which is now shown to be a mixture, and this destroys the evidence that 1-phenylacetylnaphthalene behaved differently on pyrolysis from its 4-methyl derivative.

To determine if the unsaturated centre of the indene molecule could be utilised for cyclisation, 3-β-*phenylethylindene* (XIV) was prepared from 1-hydrindone. This indene showed considerable resistance to ring closure, for only a small yield of 1 : 2-benzfluorene (chrysofluorene; XV) was obtained by dehydrogenation of the saturated product of the action of aluminium chloride or sulphuric acid on (XIV). A large proportion of the indene was converted by the cyclising reagents into resinous substances of very high boiling point,

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from introducing a fourth name and adopt the term " phenalene," which leads to the least difficulty in naming derivatives. With the system of numbering indicated, our spiran (IV) is accordingly named 7 : 8-dihydrophenalyl-7-*spirocyclo*pentane.

* Prof. L. Ruzicka has informed us privately that, when this reaction is carried out at the b. p. of carbon disulphide, chrysene is formed. In a paper shortly to be published in *Helv. Chim. Acta*, he suggests that the formation of chrysene is due to cyclisation to hexahydrochrysene, followed by dehydrogenation. In view of our experiment now recorded, it is clear that this view is untenable and that the chrysene is formed by direct *cyclo*-dehydrogenation of 1-β-phenylethylnaphthalene. That such a reaction is possible is shown by other experiments of Ruzicka, *e.g.*, the conversion of dibenzyl into phenanthrene by the conditions which gave chrysene in the case under consideration.

as in the case of the conversion of 1-benzyl*cyclo*hexanol into hexahydrofluorene (Part I, *loc. cit.*, p. 1109). In the earlier case the new ring is five-membered, but in the present

$$\text{(XIV.)} \quad \longrightarrow \quad \text{(XV.)}$$
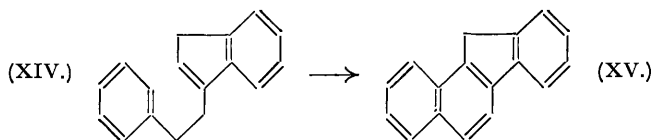
case it is six-membered, so it is clear that an explanation of the resistance to ring closure must be sought in the strained nature of the cyclisation products rather than in any increased difficulty in forming a five-membered ring. Further examples of resistance to the formation of ring systems of hexahydrofluorene type will be described in a subsequent communication.

The synthetic chrysofluorene was converted by oxidation into " chrysene ketone " (1 : 2-benzfluorenone), identical with a sample prepared by degradation of chrysenequinone (Graebe, *Annalen*, 1904, **335**, 132).

The ring system of 1 : 2-benzanthracene has also been prepared by our cyclisation method. For this purpose, 2-β-*phenylethyl*-trans-2-*decalol* was prepared from *trans*-2-decalone, dehydrated with potassium hydrogen sulphate, and the product (XVI) cyclised with aluminium chloride. The higher-boiling fractions of the resulting mixture of hydrocarbons yielded the highly crystalline *dodecahydro*-1 : 2-*benzanthracene* (XVII), which was smoothly dehydrogenated by selenium to 1 : 2-benzanthracene. There was no evidence

$$\text{(XVI.)} \qquad \text{(XVII.)} \qquad \text{(XVIII.)}$$
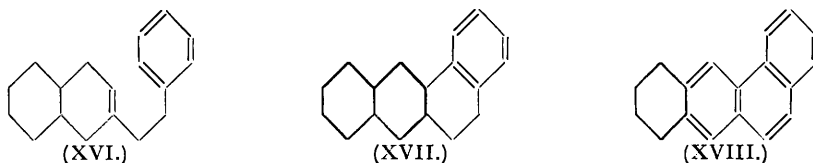
of the formation of the 3 : 4-benzphenanthrene ring system, which might arise by cyclisation of 2-β-phenylethyl-Δ$^{1:2}$-octalin (isomeric with XVI). The liquid fractions of the saturated tetracyclic compounds appeared to consist entirely of stereoisomerides of (XVII), for dehydrogenation yielded 1 : 2-benzanthracene in considerable amount. The only other picrate-forming substance present in the dehydrogenation products was 5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene* (XVIII), the constitution of which was shown by its independent synthesis by Kishner–Wolff reduction of the 5-keto-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene of Haworth and Mavin (J., 1933, 1012).

Selenium dehydrogenation of phenylethyloctalin (XVI) gave 2-β-*phenylethylnaphthalene*, which was also obtained by Kishner–Wolff reduction of 2-phenylacetylnaphthalene.

In Part I we suggested that the hydrocarbon " $C_{18}H_{16}$ " resulting from the selenium dehydrogenation of cholesteryl chloride (Diels, Gädke, and Körding, *Annalen*, 1927, **459**, 1) was essentially 1 : 2-*cyclo*pentenophenanthrene. The evidence for this was admittedly inconclusive, although there could be no doubt that the hydrocarbon obtained from cholesterol was very closely related to 1 : 2-*cyclo*pentenophenanthrene. At our request, therefore, Professor O. Diels very kindly examined a specimen of our synthetic hydrocarbon to determine whether it could be converted into the characteristic nitrogenous compound which he had obtained from the cholesterol hydrocarbon. He reported that 1 : 2-*cyclo*pentenophenanthrene was unaffected under the usual conditions, and was converted into resinous products under more drastic conditions. Moreover, no *cyclo*pentenophenanthrene was isolated from the liquors when the cholesterol hydrocarbon was converted into its nitrogenous derivative, which disposes of the possibility that the latter arises from an impurity contaminating *cyclo*pentenophenanthrene. Therefore, in view of these results and of the crystallographic measurements of Bernal and Crowfoot (*Chem. and Ind.*, 1933, **52**, 729) we agree that the hydrocarbon from cholesterol cannot be 1 : 2-*cyclo*pentenophenanthrene.

More recently, Bergmann and Hillemann (*Ber.*, 1933, **66**, 1302) synthesised 3′-methyl-

1 : 2-*cyclo*pentenophenanthrene and showed that this also closely resembles the hydrocarbon from cholesterol. Kon (Report of Chemical Society Discussion, *Chem. and Ind.*, 1933, **52**, 951) has stated that this methyl compound, which he synthesised by an adaptation of the method employed by us for the parent hydrocarbon, agrees in its crystallographic dimensions with the cholesterol product. However, the figures quoted by Bergmann and Hillemann showed a slight depression of the m. p. of the cholesterol hydrocarbon by 3'-methyl-1 : 2-*cyclo*pentenophenanthrene, and before identity can be regarded as established we consider it essential that the synthetic substance should be converted into the nitrogenous compound already mentioned.

(Addendum, February 16th, 1934.)

Complete accounts of the experiments of Professor Diels and Dr. Kon have now been published (Diels and Klare, *Ber.*, 1934, **67**, 113; Harper, Kon, and Ruzicka, this vol., p. 124). We have defined our general attitude towards their results, but deem it necessary to add the following observations concerning some details :—

(i) The only facts which are of value in establishing the non-identity of the cholesterol hydrocarbon with 1 : 2-*cyclo*pentenophenanthrene are the two which we have mentioned. The minor differences relating to crystalline form, solubility, extinction coefficients, fluorescence, etc., have very little significance. For example, both Professor Diels and Dr. Kon lay stress on the fact that *cyclo*pentenophenanthrene and the synthetic hydrocarbon of Bergmann and Hillemann crystallise in needles, whereas the cholesterol hydrocarbon and Kon's synthetic 3'-methyl compound crystallise in plates. Although pure *cyclo*pentenophenanthrene normally crystallises in needles, it will crystallise in plates from its concentrated solution in warm alcohol, the plates passing into needles on cooling. If the hydrocarbon is slightly contaminated with chrysofluorene, it *invariably* crystallises in plates.

(ii) Diels and Klare state that by repeated crystallisation from alcohol they raised the m. p. of our 1 : 2-*cyclo*pentenophenanthrene to 137—138°, whereas we recorded 134·5—135°. As we informed Professor Diels at the time, the sample which we sent to him was not material of the best quality : it was recovered from the liquors of the crystallisation of the picrate. In view of this slight discrepancy we have re-examined our pure hydrocarbon regenerated from the constant-melting picrate. Its m. p., determined with a short-stem standard thermometer, was 135—135·5°, and was completely unchanged after five recrystallisations from alcohol.

(iii) In reply to Dr. Kon's claim to priority for the type of method which we used for the synthesis of *cyclo*pentenophenanthrene, on the ground that his experiments were completed during July, 1933, we would point out that our preliminary note on the synthesis of this hydrocarbon was published on May 26th, 1933 (compare Part I, *loc. cit.*).

EXPERIMENTAL.

(Microanalyses by Dr. A. Schoeller are denoted by an asterisk.)

Methyl 4-*Nitrohemimellitate*.—(a) A mixture of 7 : 8-dihydrophenalyl-7-*spirocyclo*pentane (IV; 1·2 g.) (*i.e.*, the *trans*-1 : 2-*cyclo*pentano-1 : 2 : 3 : 4-tetrahydrophenanthrene of J., 1933, 1108), water (20 c.c.), and nitric acid (*d*, 1·42; 10 c.c.) was heated at 175—180° for 6 hours. The filtered solution was evaporated to dryness on the water-bath, the residue (0·95 g.) converted into silver salts in the usual manner, and the latter heated with methyl iodide (2 c.c.) in benzene (20 c.c.) for 24 hours. The benzene was removed from the filtered solution, and the resulting syrup was dissolved in a little alcohol and cooled. The crystalline *ester* (0·15 g.), twice recrystallised from methyl alcohol, formed long colourless needles, m. p. 143—144° [*Found : C, 49·1; H, 4·0; N, 4·9; OMe, 30·8; *M* (Rast method), 320, 328. $C_{12}H_{11}O_8N$ requires C, 48·5; H, 3·7; N, 4·6; OMe, 31·3%; *M*, 297].

(b) 4-Nitronaphthalic acid (2 g.) was oxidised as described above with nitric acid (6 c.c.) diluted with water (6 c.c.). The crude mixture of methyl esters was dissolved in alcohol (20 c.c.). After 24 hours the crystals were collected and recrystallised from methyl alcohol; they then melted at 143—144°, alone or mixed with the ester prepared as under (a). The yield was small. After several days the alcoholic mother-liquors had deposited a much larger amount of crystalline material, m. p. 83—85°. This was presumably chiefly methyl hemimellitate, but the m. p. could not be raised to the correct figure (100°) by recrystallisation.

1-(β-1'-*Naphthylethyl*)-Δ¹-cyclo*hexene and its Cyclisation Products.*

1-(β-1'-*Naphthylethyl*)cyclo*hexanol.*—This was prepared by interaction of cyclohexanone with β-1-naphthylethylmagnesium chloride, the conditions being exactly as described for the analogous experiment with cyclopentanone (J., 1933, 1107). The carbinol, b. p. 220°/7 mm. (48% yield), formed a viscous syrup which solidified when its solution in light petroleum was well cooled. After recrystallisation from light petroleum it formed a colourless powder, m. p. 60—70° (*Found : C, 85·0; H, 8·9. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%).

Synthesis of Chrysene.—The aforesaid carbinol (2·4 g.) was heated at 100° for an hour with glacial acetic acid (25 c.c.) containing concentrated sulphuric acid (2·5 c.c.). The product was freed from acid and heated with selenium (3·5 g.) at 310—330° for 18 hours. The whole was then extracted with benzene, and the filtered solution concentrated. The chrysene (0·5 g.) which crystallised was sublimed in a vacuum and recrystallised from benzene; it then formed colourless leaflets, m. p. 248—249°, alone or mixed with authentic chrysene. The molecular compound with 2 : 7-dinitroanthraquinone (from xylene) formed bright red needles, m. p. 297—298°, not depressed by a specimen prepared from authentic chrysene.

1-(β-1'-*Naphthylethyl*)-Δ¹-cyclo*hexene* was obtained in 90% yield by heating the above carbinol with potassium hydrogen sulphate (1·5 parts) at 160° for an hour. A pure sample for analysis was obtained through the picrate (m. p. 87—91°), which, however, was not obtained pure on account of dissociation. The regenerated hydrocarbon was distilled in a vacuum over sodium, and then had b. p. 167—168°/3—4 mm., $d_4^{23·5°}$ 1·0254, $n_D^{23·6°}$ 1·5993, $[R_L]_D$ 78·74 (calc., 78·60) (Found : C, 91·1; H, 8·1. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%).

7 : 8-*Dihydrophenalyl*-7-spirocyclo*hexane* (VII).—Anhydrous aluminium chloride (42 g.) was slowly added to an ice-cold solution of 1-(β-1'-naphthylethyl)-Δ¹-cyclohexene (35 g.) in carbon disulphide (350 c.c.). After being kept in ice for 7 hours with occasional shaking, the clear dark red solution was poured off from the viscous resin, shaken with water, washed, and dried over calcium chloride, and the carbon disulphide removed on the water-bath. The residue, which was completely saturated, was treated with picric acid in alcoholic solution; the picrate, twice recrystallised from alcohol, had m. p. 139—141·5° (18·5 g.). 7 : 8-*Dihydro-phenalyl*-7-spirocyclo*hexane* (VII), regenerated from this picrate and distilled in a vacuum over sodium, formed a colourless thick syrup, b. p. 176—177°/5 mm., $d_4^{23·5°}$ 1·0809, $n_D^{23·6°}$ 1·6197, $[R_L]_D$ 76·70 (calc., 76·87) (Found : C, 91·6; H, 8·3. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%). This spiran crystallised after some months, and could then be recrystallised from alcohol, forming a colourless crystalline powder, m. p. 55—56°. The *picrate*, prepared from the pure hydrocarbon, crystallised from alcohol or benzene in bright vermilion needles, m. p. 141—142° (Found : N, 8·7. $C_{18}H_{20},C_6H_3O_7N_3$ requires N, 9·0%).

The hydrocarbon mixture recovered from the original picrate mother-liquors was heated with selenium (30 g.) at 300—320° for 48 hours and yielded 4·8 g. of chrysene.

Conversion of 7 : 8-*Dihydrophenalyl*-7-spirocyclo*hexane into Pyrene.*—This was effected by heating the spiran (5 g.) with selenium (10 g.) at 320—340° for 33 hours. Liberation of hydrogen selenide was brisk at 340°, but extremely sluggish below this temperature. The black tar so formed was extracted with benzene and distilled at 5 mm. The distillate (2·4 g.) formed a pale yellow syrup and was treated, in alcohol, with picric acid (2·5 g.). The picrates were twice recrystallised from benzene and yielded 0·15 g. of dark red needles, m. p. 212—215° after re-crystallisation from alcohol, not depressed by pyrene picrate (m. p. 223°) (Found : C, 61·6; H, 3·3. Calc. : C, 61·2; H, 3·0%). The hydrocarbon regenerated from this picrate formed colourless leaflets (from alcohol), m. p. 140—144°, not depressed by pyrene, but depressed by the 1-methylpyrene, m. p. 145°, obtained from the analogous dihydrophenalyl*spirocyclo*pentane (Found : C, 94·7; H, 5·2. Calc. : C, 95·0; H, 5·0%). The colour and fluorescence changes with sulphuric acid were identical with those shown by authentic pyrene and also by the 1-methylpyrene which was formerly erroneously termed 1 : 2-cyclopentadienophenanthrene.

The benzene mother-liquors from which the pyrene picrate had crystallised were evaporated to dryness and the residue was twice recrystallised from alcohol. The resulting long vermilion needles had m. p. 140·5—141·5°, alone or mixed with the picrate of the original spiran.

cis- *and* trans-as-*Octahydrochrysenes* (VI).—1-(β-1'-*Naphthylethyl*)-Δ¹-cyclohexene (25 g.) was converted into saturated isomerides with aluminium chloride exactly as described above, and the distilled mixture of hydrocarbons (15 g.) treated with picric acid in alcohol. After separation of the picrate of the spiran (VII), the liquors were concentrated and gave a mixture of picrates which obviously contained an appreciable proportion of the picrate of the spiran. Further concentration of the liquors gave a picrate which, recrystallised thrice from methyl

alcohol, had m. p. 95—96°. This was decomposed with sodium carbonate solution, giving an oil which slowly crystallised. Two recrystallisations from alcohol gave 0·19 g. of pure (?)cis-as-*octahydrochrysene* (VI), which formed small colourless needles, m. p. 78—79° (*Found : C, 91·25; H, 8·5. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%). The pure *picrate*, prepared in methyl-alcoholic solution (2 mols. of picric acid were used), formed orange needles, m. p. 106—106·5° (*Found : C, 71·5; H, 6·0; N, 6·0. $2C_{18}H_{20},C_6H_3O_7N_3$ requires C, 71·85; H, 6·2; N, 6·0%).

For dehydrogenation to chrysene, the pure hydrocarbon (50 mg.) was heated at 300—310° with selenium (0·1 g.) in an evacuated sealed tube for 7 hours. The product, which readily crystallised, was extracted with benzene, and the solution diluted with *cyclo*hexane. The resulting crystals (10 mg.) were treated with 2 : 7-dinitroanthraquinone (11 mg.), and the molecular compound was twice recrystallised from xylene, forming scarlet needles, m. p. 293—295°, not depressed by a sample prepared from authentic chrysene.

The mother-liquors from which had been separated the above crude picrate (m. p. 95—96°) were then freed from picric acid. The resulting oil slowly deposited crystals, which were drained on a tile and twice recrystallised from methyl alcohol. The product (m. p. 105—110°) gave no picrate, but crystallised from methyl-alcoholic picric acid as the hydrocarbon, a further crystallisation from methyl alcohol giving (?)trans-as-*octahydrochrysene* (VI; 40 mg.), small colourless needles, m. p. 114—114·5° (Found : C, 91·2; H, 8·5%). The methyl-alcoholic picric acid mother-liquors deposited, on standing, 60 mg. of the picrate of the (?)cis-isomeride.

Dehydrogenation of the pure (?)trans-hydrocarbon (33 mg.) was effected by heating in an evacuated sealed tube with selenium (70 mg.) at 300—310° for 14 hours. The resulting chrysene (6 mg.) was identified by conversion into the 2 : 7-dinitroanthraquinone compound.

9-*Phenalone.*—A mixture of β-1-naphthylpropionic acid (10 g.) and anhydrous stannic chloride (15 c.c.) was heated at 120° for 3 hours. After cooling, the almost colourless clear liquid was decanted, and the dark brown solid mass was washed with water and dissolved in acetone. The solution was diluted with benzene, extracted several times with dilute hydrochloric acid to remove acetone and tin salts, and then extracted five times with concentrated hydrochloric acid (portions of 50 c.c.). The deep orange-red acid solution was diluted with water, and the crystalline precipitate collected (4 g.), washed, dried, and sublimed at 180°/3—4 mm. The sublimate was recrystallised from *cyclo*hexane, the resulting 9-phenalone (XII) forming canary-yellow crystals, m. p. 153—154° (*Found : C, 86·8; H, 4·5. Calc. : C, 86·6; H, 4·5%). This ketone gave a yellow solution with an intense green fluorescence in concentrated sulphuric acid, and yielded a purple dye when heated with methyl-alcoholic potassium hydroxide (compare D.R.-P. 283,066).

The benzene solution, after extraction of the phenalone, was shaken with dilute sodium carbonate solution, which removed 0·4 g. of unchanged acid, and then dried and distilled. The distillate, b. p. approx. 175°/3—4 mm., was dissolved in ligroin, and the solution cooled. The crystalline product (0·4 g.), recrystallised from ligroin and then from methyl alcohol, formed colourless needles, m. p. 120—121° (*Found : C, 85·65; H, 5·5. $C_{13}H_{10}O$ requires C, 85·7; H, 5·5%). This *ketone* (7 : 8-dihydro-9-phenalone or 4 : 5-benz-1-hydrindone) gave a yellow solution with a green fluorescence in concentrated sulphuric acid, and formed an *oxime* which crystallised from alcohol in colourless rhombic crystals, m. p. 226—227° (slight decomp.) (*Found : C, 79·2; H, 5·5; N, 6·8. $C_{13}H_{11}ON$ requires C, 79·1; H, 5·6; N, 7·1%).

Attempted Synthesis of Hexahydrochrysene.

γ-Phenylbutyric acid was prepared by reduction with sodium and alcohol of the mixture of phenylcrotonic acids arising from the condensation of phenylacetaldehyde with malonic acid (Vorländer, *Annalen,* 1906, **345**, 244), and was dehydrated to α-tetralone by heating with 95% sulphuric acid at 100° for an hour (yield, 27%). More recently, Horne and Shriner (*J. Amer. Chem. Soc.,* 1933, **55**, 4653) obtained a 48·7% yield of this ketone by the use of concentrated sulphuric acid at 100° for dehydration.

1-β-*Phenylethyl*-3 : 4-*dihydronaphthalene* (XIII).—α-Tetralone (17 g.) was added to an ice-cold Grignard solution prepared by the gradual addition of β-phenylethyl chloride (17 g.) in anhydrous ether (100 c.c.) to magnesium turnings (3 g.), activated with iodine. After 1½ hours at room temperature, the mixture was treated with ammonium chloride and water, and the washed ethereal solution evaporated to dryness on the water-bath. The crude liquid carbinol was heated for an hour at 160° with potassium hydrogen sulphate (30 g.), and the product fractionally distilled in a vacuum. The *dialin* (XIII) formed a colourless liquid, b. p. 209—

212°/16 mm. (yield, 10 g.), a sample for analysis being redistilled over sodium (Found : C 91·5; H, 7·7. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%).

1-β-*Phenylethylnaphthalene.*—(a) An ice-cold solution of the dialin (XIII; 8 g.) in carbo: disulphide (80 c.c.) was slowly treated with anhydrous aluminium chloride (10 g.).   Afte being kept in ice for 6 hours with occasional shaking, a test sample was shown to be completel saturated, and the clear solution was therefore decanted and worked up in the usual way yielding 4·3 g. of a viscous liquid, b. p. 218—220°/18 mm.   The amount of chrysene obtaine by dehydrogenation with selenium showed that the proportion of hexahydrochrysene in thi product could not exceed 1%.   Addition of picric acid to an alcoholic solution of the fore going liquid resulted in crystallisation of the *dipicrate* of 1-β-*phenylethylnaphthalene,* orang needles, m. p. 116—117° (*Found : C, 52·2; H, 3·2. $C_{18}H_{16},2C_6H_3O_7N_3$ requires C, 52·2 H, 3·2%).   1-β-*Phenylethylnaphthalene,* regenerated from the pure picrate and distilled ove sodium, formed a colourless viscous liquid, b. p. 175°/5 mm. (Found : C, 93·0; H, 7·0. $C_{18}H_1$ requires C, 93·05; H, 6·95%).

(b) Pure 1-phenylacetylnaphthalene, m. p. 66° (see below; 2·3 g.), was boiled under reflu: for 5 hours with amalgamated zinc (5 g.) and dilute hydrochloric acid (1 : 1; 20 c.c.), concentrate hydrochloric acid (2 c.c.) being added after each hour.   The product was extracted, dried i ethereal solution, and distilled, and gave a colourless syrup (0·6 g.) which yielded a picrate m. p. 117—118°, alone or mixed with the picrate prepared as described under (a).

Synthesis of Pyrene.

1 : 2-*Dihydrophenanthryl-4-acetic Acid* (IX).—A mixture of 4-keto-1 : 2 : 3 : 4-tetrahydro phenanthrene (39 g.), ethyl bromoacetate (33·4 g.), zinc filings (13 g.), and dry benzene (15ᵗ c.c.) was heated on the water-bath for $2\frac{1}{2}$ hours, iodine being used to activate the zinc.   Th· dark brown product was poured on ice, and the benzene layer washed with 15% sulphuric aci(and then with water.   After removal of the benzene on the water-bath, the resinous produc was heated for 2 hours with potassium hydroxide (12 g.) in methyl alcohol (150 c.c.).   Dilutioi with water precipitated 17 g. of unchanged ketone.   The filtered solution was acidified, an(the resinous precipitate recrystallised four times from acetic acid, yielding 4 g. of somewha pinkish crystals, m. p. 173—174° (Found : C, 81·0; H, 5·8. $C_{16}H_{14}O_2$ requires C, 80·7; H 5·8%).   This *acid* probably has structure (IX), although the alternative structure with aʲ extracyclic double bond is not excluded.

5-*Keto*-1 : 2 : 4 : 5-*tetrahydropyrene* (X).—The foregoing acid (1·9 g.) was heated on th water-bath for $\frac{1}{2}$ hour with 85% sulphuric acid (10 c.c.), and the solution was cooled, dilute(with water, and extracted with ether.   The ethereal extract was washed with water and dilut aqueous ammonia, and dried, and the ether removed.   The *ketone* (X) crystallised from methy alcohol in yellow plates (0·7 g.), m. p. 130—130·5° (Found : C, 87·0; H, 5·4. $C_{16}H_{12}O$ require C, 87·2; H, 5·5%).

Pyrene.—The cyclic ketone (0·7 g.) was reduced with sodium (0·3 g.) in boiling amyl alcoho (12 c.c.), and the product heated with selenium (0·5 g.) at 330—340° for 7 hours.   The crystallin· product was sublimed in a vacuum, and the sublimate converted into picrate in alcoholic solu tion.   Recrystallisation from benzene gave dark red needles, m. p. 215—218°, not depressed b pyrene picrate, and the regenerated hydrocarbon crystallised from alcohol in colourless leaflet: m. p. 142—144°, not depressed by authentic pyrene.

Chrysofluorene (1 : 2-Benzfluorene).

3-β-*Phenylethylindene* (XIV).—The condensation between α-hydrindone (26 g.) and a Grig nard solution prepared from β-phenylethyl chloride (31 g.), ether (200 c.c.), and magnesiun (5·3 g.) was effected in the customary way.   The main product (19·3 g.), b. p. approx. 165°/3— 4 mm., seemed to be largely the indene (XIV), and was heated with potassium hydrogen sulphat (1½ parts) at 160° to ensure complete dehydration of the intermediate carbinol.   A sample c 3-β-*phenylethylindene* was twice redistilled and then had b. p. 186°/9 mm. and $n_D^{18\cdot7}$ 1·598 (Found : C, 92·4; H, 7·3. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%).

Tetrahydrochrysofluorene and Chrysofluorene.—(a) When 3-β-phenylethylindene (15 g.) i carbon disulphide (150 c.c.) was treated at 0° for 16 hours with anhydrous aluminium chlorid (16 g.) there were obtained only 2·7 g. of the tetracyclic isomeride, b. p. 176°/8 mm., n_D^{18} 1·5910, the remainder being converted into resinous products of very high b. p.   *Tetrahydro chrysofluorene* formed a colourless liquid which had not crystallised after several weeks (Found C, 92·7; H, 7·5. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%).

This liquid (2 g.) was heated with selenium (2·5 g.) at 300° for 16 hours, and then at 330—340° for 14 hours. The product was distilled in a vacuum, and the semicrystalline distillate dissolved in hot acetic acid. On cooling, 0·36 g. of chrysofluorene (XV) crystallised, and had m. p. 183—184° (lit., 188°) after two recrystallisations from acetic acid (*Found : C, 94·6; H, 5·6. Calc. : C, 94·4; H, 5·6%). Oxidation with sodium dichromate in boiling acetic acid gave chrysene ketone (1 : 2-benzfluorenone), red needles, m. p. 131—132°, alone or mixed with an authentic specimen prepared from chrysenequinone.

(b) Cyclisation of 3-β-phenylethylidene (5 g.) by heating on the water-bath for an hour with acetic acid (45 c.c.) containing concentrated sulphuric acid (5 c.c.) gave substantially the same result. The saturated isomeride (0·8 g.) was dehydrogenated by selenium, and the resulting chrysofluorene, m. p. 183—184·5°, converted into its picrate, m. p. 124—126° (lit., 127·5°).

Derivatives of 1 : 2-Benzanthracene.

2-β-Phenylethyl-trans-2-decalol.—This was obtained in the usual way from *trans*-β-decalone (45 g.) and a Grignard solution prepared from β-phenylethyl chloride (42 g.). The resulting colourless syrup (43 g.), b. p. 193—194°/5—6 mm., crystallised completely after several days. For analysis, a sample of this *carbinol* was redistilled and crystallised from light petroleum, from which it separated slowly as a colourless microcrystalline powder, m. p. 54—59° (Found : C, 83·6; H, 10·05. $C_{18}H_{26}O$ requires C, 83·7; H, 10·15%). In this case, treatment with sulphuric acid in acetic acid was not a suitable procedure for ring closure, for the yield of hydrocarbon was poor (3·7 g. from 10 g. of carbinol) and the product was appreciably unsaturated. Dodecahydro-1 : 2-benzanthracenes were, however, present in the products, for selenium dehydrogenation gave 1·1 g. of pure 1 : 2-benzanthracene, identified by mixed m. p., colour reaction with sulphuric acid, and oxidation to 1 : 2-benzanthraquinone.

2-β-Phenylethyl-$\Delta^{2:3}$-octalin (XVI).—The distilled, but not recrystallised, carbinol was dehydrated by heating with potassium hydrogen sulphate (2 parts) at 170—180° for 2 hours. The dehydration proceeded with less facility than in other cases. An intermediate fraction of the product was redistilled over sodium. The *octalin* (XVI) had b. p. 155°/3—4 mm., $n_D^{18.7}$ 1·5402, and absorbed the amount of bromine required for one double bond (Found : C, 89·6; H, 10·0. $C_{18}H_{24}$ requires C, 89·9; H, 10·1%).

Dodecahydro-1 : 2-benzanthracene (XVII).—The β-phenylethyloctalin (XVI; 35 g.) was treated in the normal way with aluminium chloride (44 g.) in carbon disulphide (350 c.c.). After being kept in ice for 4 hours and then over-night at room temperature, the completely saturated product was worked up and distilled at 4—5 mm. into 3 fractions : (I) b. p. 158—160° (13·8 g.); (II) b. p. 160—170° (6·3 g.); (III) b. p. 175—179° (11·6 g.). Fraction I was a colourless syrup which deposited some long needles after several days. Fraction II crystallised slowly, whereas fraction III crystallised very rapidly. Fractions II and III were combined, and the crystals drained free from oil. Recrystallisation from methyl alcohol gave 4 g. of *dodecahydro-1 : 2-benzanthracene* (XVII), a further 1 g. being obtained subsequently from fraction I. The pure hydrocarbon formed long colourless needles, m. p. 71—72° (Found : C, 90·0; H, 10·2. $C_{18}H_{24}$ requires C, 89·9; H, 10·1%). Dehydrogenation with selenium (2 parts) at 320—330° gave pure 1 : 2-benzanthracene in 50% yield.

After standing for a week, the liquid portion of fraction I was separated from crystals and redistilled over sodium. Analysis of an intermediate fraction, b. p. 158—160°/3—4 mm., showed that this contained only isomerides of dodecahydro-1 : 2-benzanthracene (Found : C, 89·9; H, 10·1%). This liquid (7·2 g.) was heated with selenium (16 g.) at 300—320° for 48 hours. The product was extracted with benzene, and the filtered solution concentrated and treated with alcohol. 1 : 2-Benzanthracene (2·1 g.) crystallised. The mother-liquors were freed from benzene, dissolved in xylene (50 c.c.), and heated under reflux for an hour with maleic anhydride (5 g.) in order to remove the remainder of the 1 : 2-benzanthracene. The unattacked material (2·5 g.) was recovered by removal of the xylene in steam in presence of excess of alkali, and was treated with picric acid (2·5 g.) in alcohol. The resulting *picrate* (0·75 g.) formed orange needles, m. p. 155° (*Found : C, 62·65; H, 4·1. $C_{18}H_{16},C_6H_3O_7N_3$ requires C, 62·7; H, 3·7%). Treatment with sodium carbonate solution led to a *hydrocarbon* which separated from alcohol in colourless plates, m. p. 89—90° (*Found : C, 93·2; H, 6·9. $C_{18}H_{16}$ requires C, 93·05; H, 6·95%). When it was first obtained it was thought that this hydrocarbon was 2-β-phenylethylnaphthalene, with which it is isomeric. This was shown to be incorrect by the formation of a different compound by reduction of 2-phenylacetylnaphthalene (below). The true nature of the hydrocarbon just described was shown by (a) its dehydrogenation by

selenium to 1 : 2-benzanthracene, and (b) the formation of the same 5 : 6 : 7 : 8-*tetrahydro-1 : 2-benzanthracene* (XVIII) by reduction of its 5-keto-derivative (Haworth and Mavin, *loc. cit.*). For this purpose, the ketone was converted into its semicarbazone in boiling aqueous-alcoholic solution, and the semicarbazone (m. p. 283—284°; 1·5 g.) heated at 175—180° for 3 hours with a solution of sodium ethoxide (1·5 g. of sodium in 25 c.c. of alcohol). Some semi-carbazone remained unattacked, but was readily separated by its sparing solubility in alcohol. The alcoholic extract yielded a picrate identical with that obtained by dehydrogenation of the mixture of dodecahydrobenzanthracenes, the identification being completed by the isolation of the hydrocarbon from its pure picrate.

In another experiment the crude mixture of dodecahydrobenzanthracenes (8·7 g.) formed by aluminium chloride cyclisation of phenylethyloctalin gave 3·1 g. of 1 : 2-benzanthracene and 1·9 g. of the picrate of 5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene. There was no indication of the presence in the liquors of 3 : 4-benzphenanthrene picrate, which forms characteristic bright red needles (Cook, J., 1931, 2528).

1- *and* 2-*Phenylacetylnaphthalenes.*

The Friedel–Crafts condensation between naphthalene (50 g.) and phenylacetyl chloride (60 g.) by means of anhydrous aluminium chloride (100 g.) was effected in carbon disulphide (400 c.c.) at 0° (compare Graebe and Bungener, *loc. cit.*). The product was distilled in a vacuum (b. p. 220—221°/3—4 mm.) and recrystallised from methyl alcohol, giving 45 g. of colourless plates, m. p. 55—58°. This material (7·5 g.) gave 1·8 g. of the semicarbazone of 2-phenyl-acetylnaphthalene, showing the presence of at least 20% of the β-naphthyl ketone in the mixture.

Separation of Isomerides.—The mixture of ketones (10 g.) was treated with picric acid (10 g.) in hot alcoholic solution. The crystals which separated were recrystallised from alcohol and collected while still warm. An additional crystallisation gave the pure *picrate* of 2-*phenylacetylnaphthalene*, pale lemon-yellow needles, m. p. 143—144° (*Found : N, 8·7. $C_{18}H_{14}O,C_6H_3O_7N_3$ requires N, 8·8%). The regenerated ketone, recrystallised from methyl alcohol, had m. p. 99—100°, alone or mixed with authentic 2-phenylacetylnaphthalene (Cook, J., 1931, 2015). Its *semicarbazone* separated from alcohol, in which it was very sparingly soluble, in small colourless crystals, m. p. 203—205° (*Found : N, 13·4. $C_{19}H_{17}ON_3$ requires N, 13·9%).

The picrates which separated from the liquors were recrystallised from alcohol, giving the *picrate* of 1-*phenylacetylnaphthalene*, canary-yellow needles, m. p. 99—100° (*Found : N, 8·7%). From this was obtained pure 1-*phenylacetylnaphthalene* in large colourless plates (from methyl alcohol), m. p. 66—67° (Found : C, 87·7; H, 5·8. $C_{18}H_{14}O$ requires C, 87·8; H, 5·7%). The easily soluble *semicarbazone* of this ketone formed small colourless crystals (from alcohol), m. p. 162—163° (*Found : N, 13·5%).

2-β-*Phenylethylnaphthalene.*—(a) 2-Phenylacetylnaphthalene semicarbazone (1·65 g.) was heated at 180—190° for 6 hours with a solution of sodium ethoxide (1·65 g. of sodium in 20 c.c. of alcohol). The whole was diluted with water, and the crystalline product collected and twice recrystallised from alcohol. 2-β-*Phenylethylnaphthalene* formed colourless microscopic needles, m. p. 99—100° (Found : C, 93·2; H, 6·9. $C_{18}H_{16}$ requires C, 93·05; H, 6·95%). Its picrate was too readily dissociated to be obtained pure.

(b) The same hydrocarbon was obtained by selenium dehydrogenation of 2-β-phenylethyl-$\Delta^{2:3}$-octalin (XVI), the crude product being purified through the picrate.

SUMMARY.

(1) A detailed study has been made of the cyclisation of 1-(β-1′-naphthylethyl)-Δ^1-*cyclo*pentene and 1-(β-1′-naphthylethyl)-Δ^1-*cyclo*hexene and the nature of the products has been elucidated.

(2) One of the principal products in each case is a spiran which undergoes a rearrangement during selenium dehydrogenation. This emphasises the caution necessary when assigning structures to compounds on the basis of their selenium dehydrogenation products.

(3) The cyclisation of suitable unsaturated compounds containing an aromatic nucleus has been shown to be applicable also for the synthesis of hydroaromatic compounds containing the ring systems of chrysene, chrysofluorene, and 1 : 2-benzanthracene.

(4) Considerable resistance to ring formation is offered when the new ring system con-

tains a hydrogenated six-membered ring fused to the five-membered ring of the hydrindene system.

(5) The method fails when the unsaturated compound to be cyclised is of the dihydro-aromatic type, in which case simple dehydrogenation occurs.