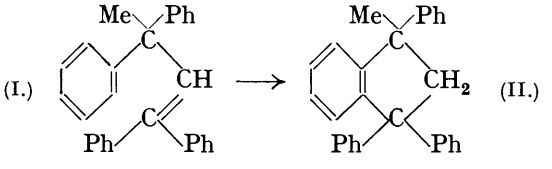
262. *The Synthesis of Compounds related to the Sterols, Bile Acids, and Oestrus-producing Hormones. Part I.* 1 : 2-cyclo*Pentenophenanthrene.*

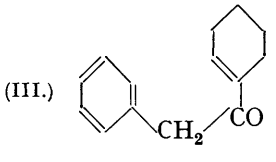
By J. W. Cook and C. L. Hewett.

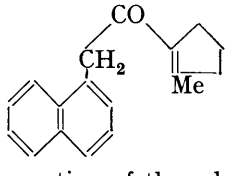
The structures of the two dimerides of *as.*-diphenylethylene have been conclusively established by Bergmann and Weiss (*Annalen*, 1930, **480**, 49) as $\alpha\alpha\gamma\gamma$-tetraphenyl-Δ^{α}-butene (I) and 1 : 3 : 3-triphenyl-1-methylhydrindene (II), and the remarkable ease with which (I) is converted into (II) suggested to us that this type of cyclisation of aromatic



olefins might prove of general application as a synthetic method for compounds containing condensed ring systems. Such a method would be adaptable to the synthesis of compounds closely related to the sterols, bile acids, and oestrins, for which existing methods of phenanthrene-ring synthesis are unsuitable. The synthesis of naphthalene derivatives by a method similar to that now described has been accomplished by Darzens (*Compt. rend.*, 1926, **183**, 748; 1930, **190**, 1562).

With stannic chloride as a condensing agent (cf. *idem*, *ibid.*, 1910, **150**, 707), phenylacetyl chloride reacted with *cyclo*hexene, and 1-naphthylacetyl chloride with 1-methyl-Δ^{1}-*cyclo*pentene, to give addition products which were converted by hot dimethylaniline into 1-*phenylacetyl*-Δ^{1}-cyclo*hexene* (III) and 1-α-*naphthylacetyl*-2-*methyl*-Δ^{1}-cyclo*pentene*





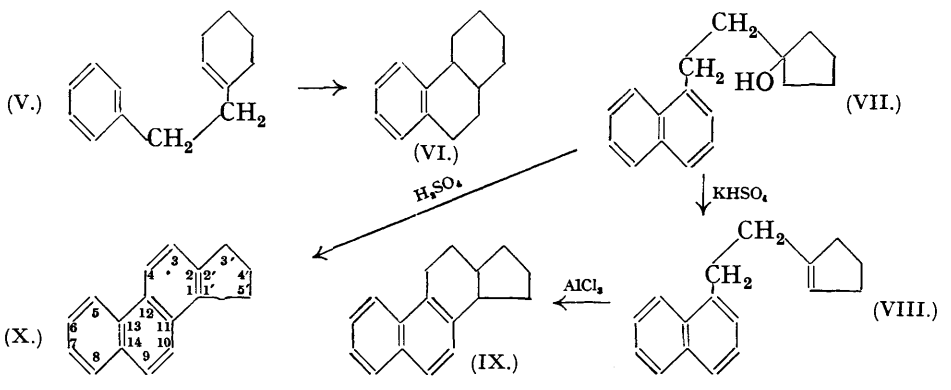
(IV) respectively. The conditions used for the preparation of these ketones might well have given the corresponding phenanthrene derivatives, and perbenzoic acid titrations

were used to distinguish between these alternative structures. The titrations clearly indicated the presence of a double bond in each case, so structures (III) and (IV) are correct. Further evidence was provided by the fact that selenium dehydrogenation of the product of the action of methylmagnesium iodide on (III) furnished no 9-methylphenanthrene, which should have been smoothly formed if the tricyclic structure were correct.

All attempts to effect direct conversion of (III) into the corresponding keto-octahydrophenanthrene have failed (see p. 1106). The inhibiting influence of the ketonic group was undoubtedly responsible for this failure, for when the ketone (III) was reduced by Clemmensen's method, and the product dehydrogenated with selenium, phenanthrene was formed. Hence cyclisation had occurred at some stage of the process.

Accordingly, oxygen-free compounds analogous to (III) and (IV) were next investigated, with very successful results. 1-β-*Phenylethyl*-Δ^1-cyclo*hexene* (V) was obtained by dehydration of the *carbinol* resulting from *cyclo*hexanone and β-phenylethylmagnesium chloride. This hydrocarbon was readily converted under a variety of conditions into 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (VI),* the constitution of which followed from the fact that it was saturated towards bromine and was smoothly dehydrogenated to phenanthrene. This octahydrophenanthrene had been obtained by Bardhan and Sengupta (J., 1932, 2520) by a somewhat similar method (we are indebted to Dr. R. D. Haworth for drawing our attention to this paper which we had overlooked), but as Bogert (*loc. cit.*) has pointed out, the present method is much simpler than that of Bardhan and Sengupta, and also demonstrates the true nature of the cyclisation process, which was apparently unsuspected by the Indian authors.

In a similar manner, the Grignard compound of β-1-*naphthylethyl chloride* was condensed with *cyclo*pentanone to yield a *carbinol* (VII) which was dehydrated by potassium hydrogen sulphate to give 1-(β-1′-*naphthylethyl*)-Δ^1-cyclo*pentene* (VIII), and this olefin was isomerised



by aluminium chloride or stannic chloride into 1 : 2-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IX).† Cyclisation of both of the hydrocarbons (V and VIII) takes place

* After the publication of our preliminary communication (*Chem. and Ind.*, May 26th, 1933), describing the work now recorded, Col. M. T. Bogert was good enough to send us a copy of his note (*Science*, March 17th, 1933) announcing the synthesis of this octahydrophenanthrene by a method apparently identical with our own, except that phenylethyl bromide was used where we used the chloride. No experimental details have been published by Col. Bogert, and we therefore include an account of our own experiments in the present communication.

† In consequence of Richter's use of the term " naphthindene " for what would now be called a benzindene, our hydrocarbon (IX) cannot be called, as it should be, a hexahydronaphthindene. Moreover, it seems undesirable to perpetuate any of the numerous anomalies of this type introduced by Richter, so we refrain from using the term benzonaphthindene. Since (X) is a fusion of a *cyclo*pentene and a phenanthrene ring, Ruzicka's use (*Helv. Chim. Acta*, 1933, **16**, 833) of the name *cyclo*pentanophenanthrene for this compound seems illogical, and we adhere to the nomenclature already used by one of us (J., 1931, 2529) for similar fused *cyclo*pentene rings.

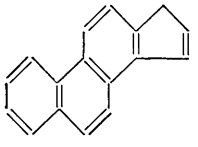
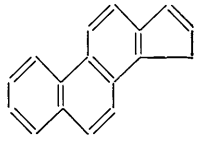
with the utmost ease, and it is of interest that every stage of the synthesis of (IX) from α-bromonaphthalene may be effected at room temperature. The ring system of (IX) is that which is now known to be present in the sterols, the bile acids, and the ovarian hormone.

The cyclisation of naphthylethyl*cyclo*pentene (VIII) by anhydrous aluminium chloride was effected under conditions which suffice for the complete conversion of *cis*- into *trans*-decalin (Zelinsky and Turowa-Pollak, *Ber.*, 1932, **65**, 1299; cf. *ibid.*, 1929, **62**, 1658), so the chief product of the reaction, readily obtained pure through the medium of its well-crystallised *picrate*, is probably the *trans*-isomeride of (IX), in which the five-membered ring is joined to the adjacent six-membered ring by *trans*-linkages. The configuration of these two rings appears to be the same, therefore, as that of the corresponding rings in the sterols and bile acids (Wieland and Dane, *Z. physiol. Chem.*, 1933, **216**, 91). The structures assigned to the compounds (VIII) and (IX) are in agreement with their chemical behaviour and optical properties, although at present there is no positive evidence that (IX) is not the alternative *spirocyclic* compound which might be formed by six-membered ring-closure at position 8 of the naphthalene system. This possibility in no way invalidates the structure assigned to 1 : 2-*cyclo*pentenophenanthrene (below).

Ring closure of 1-β-phenylethyl*cyclo*hexene (V) was most conveniently effected by sulphuric acid in acetic acid at 100°, but when this procedure was adopted with (VIII) the acid caused dehydrogenation, sulphur dioxide being liberated with the formation of 1 : 2-cyclo*pentenophenanthrene* (X). It was not necessary to isolate the hydrocarbon (VIII), for (X) was obtained directly from the carbinol (VII) by warming with sulphuric acid in acetic acid. Indeed, this operation forms an extremely convenient method of preparation of 1 : 2-*cyclo*pentenophenanthrene.

The selenium dehydrogenation of condensed-ring compounds of known structure containing five-membered rings has not hitherto been studied, and the behaviour of the compounds now described presents many points of interest. The following are briefly the facts.

(i) The pure *trans*-hydrocarbon (IX) was scarcely attacked by selenium at 300—320° during 24 hours. Above 330°, hydrogen selenide was readily liberated, and at 330—340° dehydrogenation proceeded smoothly with the formation of a ***hydrocarbon***, $C_{17}H_{12}$, probably (XI) or (XII). There was no evidence of the intermediate formation of

(XI.)   (XII.)

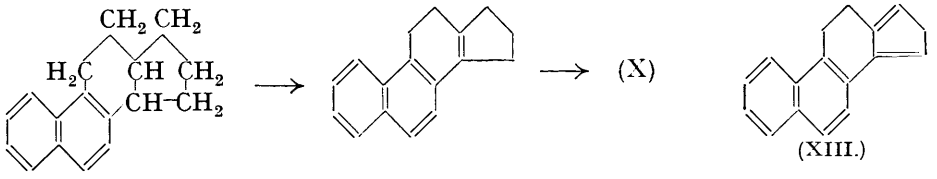
the *cyclo*pentenophenanthrene (X), for when the selenium treatment was curtailed, only the indene compound (XI or XII) and the original hydrocarbon (IX) were isolated, and a careful search failed to reveal the presence of any of the hydrindene compound (X).

(ii) Selenium dehydrogenation (at 305—325°) of the mixture of hydrocarbons obtained by the action of stannic chloride on 1-(β-1′-naphthylethyl)*cyclo*pentanol (VII) or of the saturated, but non-picrate-forming, constituents of the crude mixture containing the *trans-cyclo*pentanotetrahydrophenanthrene (IX) formed by the action of aluminium chloride on (VIII) led to crystalline hydrocarbon mixtures from which 1 : 2-*cyclo*pentenophenanthrene (X) was readily isolated by purification through the *s*-trinitrobenzene complex.

(iii) Pure 1 : 2-*cyclo*pentenophenanthrene (X) was recovered completely unchanged after treatment with selenium at 340° for 12 hours. There was no trace of the indene compound (XI or XII), which forms a characteristic sparingly soluble dark red picrate, and should have been readily detected if present. This is in agreement with the observations of Ruzicka and Thomann (*Helv. Chim. Acta*, 1933, **16**, 224), who were unable to dehydrogenate the "$C_{18}H_{16}$" hydrocarbon from cholesterol, for it is shown (p. 1103) that this hydrocarbon probably consists essentially of 1 : 2-*cyclo*pentenophenanthrene. It may be remarked that similar failure to dehydrogenate such a five-membered ring-system

had been anticipated and observed by one of us (J. W. C.) in the analogous case of 5 : 6-*cyclo*penteno-1 : 2-benzanthracene before he suggested to Dr. Rosenheim and his collaborators at a meeting of the Biochemical Society (December 16th, 1932) that the "$C_{18}H_{16}$" compound from cholesterol was 1 : 2-*cyclo*pentenophenanthrene.

At first sight, these three sets of observations seem somewhat conflicting, but we believe that there is a simple stereochemical explanation which we advance provisionally as seeming the only satisfactory interpretation of the facts. The mixtures referred to under (ii) probably contain *cis-cyclo*pentanotetrahydrophenanthrene (IX) which readily loses the two hydrogen atoms attached to the tertiary carbon atoms, giving a tetrahydroindene compound, which smoothly passes into the hydrindene compound (X). With the *trans-cyclo*pentanotetrahydrophenanthrene the case is rather different. Here,



the two tertiary hydrogen atoms are remote from one another; elimination is less readily effected, but when it does take place, *four* hydrogen atoms are eliminated *in pairs* (*e.g.*, at 2′ : 3′ and 1′ : 5′) to give a compound such as (XIII), which subsequently undergoes further dehydrogenation and rearrangement. The important point is that in this way removal of hydrogen from the five-membered ring is initiated. Differences in chemical behaviour between cyclic stereoisomerides are, of course, well known, one interesting example having been previously observed by one of us in the case of *cis*- and *trans*-1 : 5-dichloro-9 : 10-dihydroanthraquinols (Barnett, Cook, and Matthews, *Rec. trav. chim.*, 1925, **44**, 728).

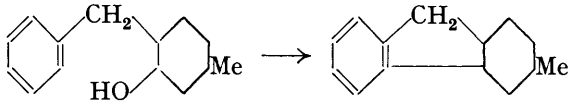
The obvious objection to this explanation, *viz.*, that cholesterol, which apparently contains the corresponding rings also locked in the *trans*-position (Wieland and Dane, *loc. cit.*), gives the hydrindene (X) and not the indene (XI or XII), is readily answered when it is realised that in this case the middle six-membered ring is reduced so that the hydrogen atom (or methyl group) at position 1 may be eliminated with the methyl group (or hydrogen atom) at position 11 (scheme of numbering on p. 1099). Hence there is no necessity for the five-membered ring to be involved.

The prototropic mobility of the indene system, definitely established by the identity of 5- and 6-methoxyindenes (Ingold and Piggott, J., 1923, **123**, 1469), would suggest that (XI) and (XII) represent tautomeric forms of the same substance. It is now recognised, however, that the *p*-methoxy-group greatly facilitates such prototropic changes (compare Shoppee, J., 1931, 1225), so that the system (XI) $\rightleftharpoons$ (XII) is probably less mobile than the one investigated by Ingold and Piggott, and the two structures may represent different substances, one of them possibly convertible into the other as in the case of 1- and 3-benzylindenes (Courtot, *Compt. rend.*, 1915, **160**, 523), and 1 : 2- and 1 : 3-diphenylindenes (García Banús and Calvet, *Anal. Fís. Quím.*, 1929, **27**, 49). This may be the explanation of the fact that, in addition to the hydrocarbon $C_{17}H_{12}$, m. p. 143° (*picrate*, m. p. 192°), there was also formed by the dehydrogenation of the *trans*-tetrahydro-compound (IX) a smaller yield of a substance, m. p. 68—70° (picrate, m. p. 208—209°). Both compounds gave the same series of colour and fluorescence changes with concentrated sulphuric acid, and their inter-relationship is being further examined. If it be accepted that these two substances are represented by formulæ (XI) and (XII), then it follows that neither the hydrocarbon, m. p. 239—240°, obtained from cholesterol by Ruzicka and Thomann (*loc. cit.*), nor the hydrocarbon, m. p. 243°, obtained from oestrin by Butenandt (*Angew. Chem.*, 1932, **45**, 655) can have these structures.

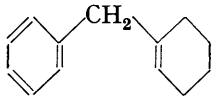
Analogous reactions to those described above have been carried out using *cyclo*hexanone instead of *cyclo*pentanone. Thus, the action of sulphuric acid in acetic acid on 1-(β-1′-naphthylethyl)*cyclo*hexanol (corresponding with VII) resulted in an oil from which chrysene

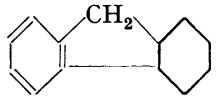
was obtained by dehydrogenation with selenium. Moreover, the action of aluminium chloride on the dehydration product of this carbinol (corresponding with VIII) led to a mixture from which the sparingly soluble, highly coloured picrate (m. p. 141—142°), presumably of *trans-as.*-octahydrochrysene, was obtained. These experiments, which are not yet complete, will be described in a future communication.

The ease with which the formation of the six-membered ring takes place with the hydrocarbons (V) and (VIII) suggested that a similar reaction might be utilised for the synthesis of fluorene derivatives. Two examples of this have already been given by Wallach (*Ber.*, 1896, **29**, 2962; *Annalen*, 1899, **305**, 261), who obtained saturated hydrocarbons by dehydration of 6-benzyl-3-methyl*cyclo*hexanol and benzylmenthol. He failed to recognise the true nature of the reaction and represented it as ring closure by dehydration, *e.g.*,



It seems clear that the initial product of the reaction was the *cyclo*hexene derivative, which subsequently isomerised to the fluorene derivative, for we found that 1-benzyl*cyclo*hexanol was converted under the same conditions (phosphoric oxide at 160°) into a saturated hydrocarbon which can be formulated only as *hexahydrofluorene* (XV).

(XIV.) 



(XV.)

It is noteworthy that cyclisation of benzyl*cyclo*hexene (XIV) could not be effected by stannic chloride or aluminium chloride at room temperature or by sulphuric acid in acetic acid at 100°, conditions which sufficed for facile closure of the six-membered ring in the case of (V) and (VIII). Under all of these conditions the olefin (XIV) was either unaltered or largely converted into high-boiling resinous products. The constitution of the unsaturated dehydration product of 1-benzyl*cyclo*hexanol as 1-benzyl-Δ^1-*cyclo*hexene (XIV) has been established with certainty by von Auwers and Treppmann (*Ber.*, 1915, **48**, 1218), so its failure to undergo cyclisation cannot be explained by assuming that the double bond is extracyclic.

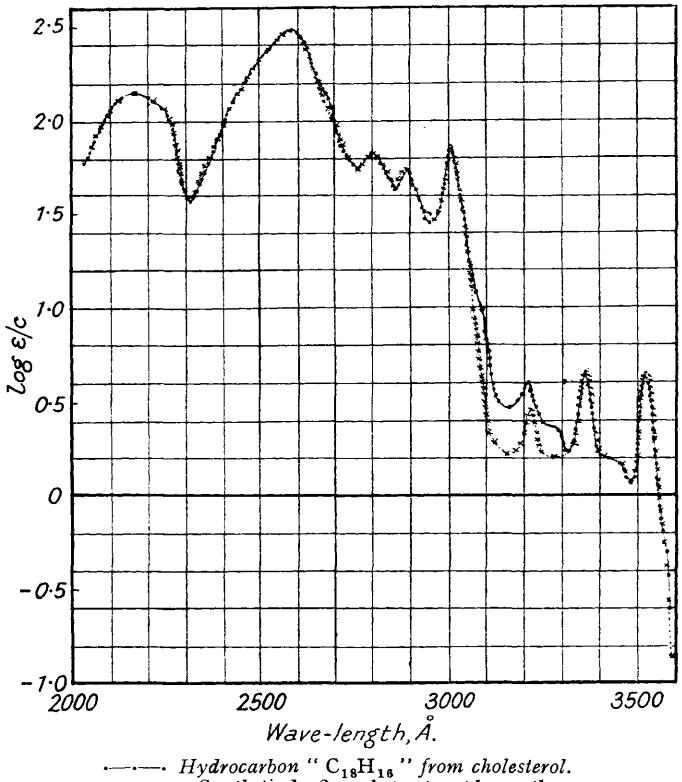
The formation of the five-membered ring in (II) from the olefin (I) takes place very readily, so the experiments now recorded provide confirmation of the fact that five-membered rings are much less readily formed than six-membered rings when the new ring is situated between two cyclic systems. It was lack of appreciation of this fact that led to the original erroneous conclusion that " Ring II " of the sterols and bile acids was five-membered, the fallacy of this conclusion being first pointed out by Rosenheim and King (*Chem. and Ind.*, 1932, **51**, 464).

Attempts to obtain fluorene by dehydrogenation of the hexahydro-compound (XV) were unsuccessful; failure of the selenium treatment was probably due to the comparatively low boiling point of the hydrocarbon, which did not permit of the attainment of a sufficiently high temperature for dehydrogenation to occur. Doubtless this difficulty will disappear in the case of the more complex fluorene derivatives which it is hoped to synthesise by the same type of method.

The synthesis of 1 : 2-*cyclo*pentenophenanthrene (X) was undertaken in order to compare it with the hydrocarbon " $C_{18}H_{16}$ " obtained by the selenium dehydrogenation of cholesterol or cholesteryl chloride (Diels, Gädke, and Körding, *Annalen*, 1927, **459**, 1), of ergosterol (Diels and Karstens, *Annalen*, 1930, **478**, 129), and of cholic acid (Ruzicka and Thomann, *Helv. Chim. Acta*, 1933, **16**, 224). On the basis of the new sterol and bile acid formulation (Rosenheim and King, *Chem. and Ind.*, 1932, **51**, 464, 954; Wieland and Dane, *Z. physiol. Chem.*, 1932, **210**, 268), it seemed probable that " $C_{18}H_{16}$ " was really *cyclo*pentenophenanthrene, $C_{17}H_{14}$ (compare Rosenheim and King, *Chem. and Ind.*, 1933, **52**, 301), and we have already suggested (*ibid.*, p. 451) that our preliminary comparison of

the two hydrocarbons lent support to this view. We are now definitely of the opinion that the hydrocarbon from cholesterol (which we have obtained appreciably purer than Diels's sample but still not quite pure) consists essentially of 1 : 2-*cyclo*pentenophenanthrene (X). By a new dehydrogenation experiment in which cholesteryl chloride was heated with selenium for 120 hours, the temperature being kept strictly within the limits 320—340°, we obtained a specimen of "$C_{18}H_{16}$" which, after purification through the picrate and *s*-trinitrobenzene complex, gave the following m. p. and mixed m. p. values:

Compound.	"$C_{18}H_{16}$" from cholesterol.	1 : 2-*cyclo*Pentenophenanthrene.	Mixed m. p.
Hydrocarbon	131—133° (sinters 129°)	134·5—135°	131—133°
Picrate	123·5—124·5	134·5—135	124—127
s-Trinitrobenzene complex	148—149·5	166—167	151—154



·—·—· *Hydrocarbon "$C_{18}H_{16}$" from cholesterol.*
x—x—x *Synthetic* 1 : 2-cyclo*pentenophenanthrene.*

The two hydrocarbons have also been examined spectroscopically, and their absorption curves are here reproduced, the following being the wave-lengths of the maxima (Å.) : *

Cholesterol hydrocarbon	2167	2584	2795	2887	3007	3209	3359	3518
Synthetic *cyclo*pentenophenanthrene	2165	2586	2798	2883	3007	3211	3360	3518

The inaccessibility of the hydrocarbon from cholesterol in appreciable quantity has rendered it impracticable to attempt to devise methods for the complete removal of the persistent impurity.

The dehydrogenation of cholesteryl chloride can be considerably accelerated by using a slightly higher temperature (340—360°), but it is then much more difficult to isolate the

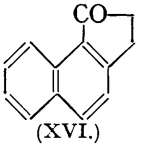
* Dr. J. D. Bernal has been so good as to make an *X*-ray crystallographic comparison of the two hydrocarbons. He will describe this elsewhere, but it should be stated here that the results do not appear to support our conclusion. We would point out, however, that the hydrocarbon from cholesterol has not yet been obtained in a state of purity, and in comparisons of this nature the possible influence of the unknown impurity must be taken into account.

hydrocarbon "$C_{18}H_{16}$" in a state approaching purity. In fact, in one such experiment, purification of the crystalline product through the picrate and the *s*-trinitrobenzene complex led to a substance, m. p. 230—233° (after sintering), which seemed to be impure chrysene. Chrysene was obtained by Diels and Karstens (*loc. cit.*) as the chief product of the selenium dehydrogenation of cholic acid, whereas Ruzicka and Thomann (*loc. cit.*) failed to isolate any chrysene. The discrepancy between these two observations is possibly due to the use of a somewhat higher temperature by the first two authors, with consequent molecular rearrangement. There seems no doubt that cholesterol gives chrysene when dehydrogenated at higher temperatures by agents other than selenium (Diels and Gädke, *Ber.*, 1927, **60**, 140; Raudnitz, Petrů, and Stadler, *Ber.*, 1933, **66**, 879).

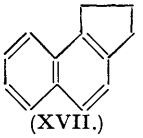
We have confirmed the findings of Diels, Gädke, and Körding that chromic acid oxidation of the "$C_{18}H_{16}$" hydrocarbon from cholesterol gives no definite product, and we have been unable to obtain any evidence of the formation of an *o*-quinone by oxidation of this hydrocarbon or of synthetic *cyclo*pentenophenanthrene. It appears that oxidation of the five-membered ring takes place with much the same ease as oxidation of the phenanthrene system, with consequent profound breakdown of the molecule. 1 : 2-*cyclo*-Pentenophenanthrene thus occupies an intermediate position between 4 : 5-benzhydrindene, which is smoothly oxidised in the five-membered ring without attack of the naphthalene system, giving 4 : 5-benz-3-hydrindone * (XVI; Kruber, *Ber.*, 1932, **65**, 1389), and the *cyclo*penteno-1 : 2-benzanthracenes, which are unattacked in the five-membered ring and pass readily into the *cyclo*penteno-1 : 2-benzanthraquinones (Cook, J., 1931, 2529). The failure to isolate a quinone from 1 : 2-*cyclo*pentenophenanthrene is thus in harmony with the well-known fact that the *meso*-positions of the phenanthrene system are less reactive than the corresponding positions of the anthracene system.

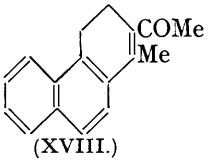
By the action of pyridine on the nitrogen peroxide adduct of the "$C_{18}H_{16}$" hydrocarbon from cholesterol, Diels, Gädke, and Körding isolated a nitrogenous compound, $C_{18}H_{13}O_2N$, which they suggested, chiefly on the basis of ultimate analysis, was not a nitro-compound but a nitroso-ketone. This assumption is unnecessary if the hydrocarbon is really $C_{17}H_{14}$, and the reaction may now be interpreted as addition of nitrogen dioxide, followed by loss of nitrous acid with the formation of a nitro-derivative of the original hydrocarbon ($C_{17}H_{13}O_2N$).

Before the synthetic methods which have been described had been worked out, other possible routes to compounds containing the *cyclo*pentenophenanthrene ring system had been explored. Haworth, Letsky, and Mavin (J., 1932, 1784) had shown that succinic anhydride condensed with 2-methylnaphthalene in position 6, so that it seemed possible that 4 : 5-benz-3-hydrindone (XVI) would likewise condense with succinic anhydride in the corresponding position of the naphthalene system, in which case the desired ring system could have been attained by reduction and then cyclisation.



(XVI.)


(XVII.)



(XVIII.)

No condensation between 4 : 5-benz-3-hydrindone (XVI) and succinic anhydride in presence of aluminium chloride occurred at normal or slightly elevated temperatures, whereas at higher temperatures only dark-coloured resinous products were formed. This failure to condense under normal conditions is in accord with the view already expressed (this vol., p. 399) that substitution of 2-methylnaphthalene in position 6 is due to primary entry of the substituent into position 1, followed by migration; for, in the case now under consideration, position 1 is already occupied and such a mechanism could not prevail.

4 : 5-Benz-3-hydrindone (XVI) was readily formed by dehydration of β-2-naphthylpropionic acid with stannic chloride, a procedure which renders the cyclic ketone much

* In these reduced rings, we do not adhere to the naphthindene convention (see footnote, p. 1099) for the unreduced indene ring.

more accessible than the method of Mayer and Sieglitz (*Ber.*, 1922, **55**, 1855). By Clemmensen reduction, this ketone was converted into 4 : 5-benzhydrindene (XVII), which was required for spectroscopic study. This hydrocarbon has not hitherto been prepared synthetically, although Kruber (*loc. cit.*) has recently isolated it from coal tar.

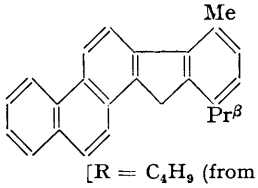
Another possible method of synthesis of compounds of the type we were seeking seemed to be provided by an adaptation of the reaction of Kon and Qudrat-i-Khuda (J., 1926, 3071), who showed that 1-acetyl-Δ^1-*cyclo*hexene condensed with ethyl sodiomalonate to give a derivative of 1 : 3-diketodecalin. Such a reaction with 2-acetyl-1-methyl-3 : 4-dihydrophenanthrene (XVIII) would give rise to a hydrogenated chrysene derivative in which degradation of the new six-membered ring to a five-membered ring might have been achieved. Unfortunately, the only crystalline product obtained by the action of acetyl chloride on 1-methyl-3 : 4-dihydrophenanthrene (a crystalline solid, m. p. 82—83°; compare Haworth, J., 1932, 1130) was 1-methylphenanthrene, which was evidently formed by dehydrogenation at the expense of the stannic chloride used as a condensing agent. This experiment is typical of the difficulties, due to the marked tendency for the reduced ring to become aromatic, which we have encountered during many attempts to build up the desired ring system from 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene. We hope eventually to overcome these difficulties by the use of analogous derivatives of *as.*-octahydrophenanthrene.

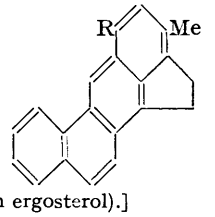
The compounds described in this communication are being tested for various types of biological activity, and the new synthetic methods are being extended to the production of more complex compounds containing the *cyclo*pentenophenanthrene ring system, and also to other types of condensed ring systems.

Note.—After the foregoing introduction had been written, two papers appeared by Ruzicka and his collaborators (*Helv. Chim. Acta*, 1933, **16**, 812, 833). These were submitted for publication on May 31st and June 1st, respectively. The first paper deals with the dehydrogenation of cholesterol, ergosterol, and cholic acid, and the second with the synthesis of 1 : 2-*cyclo*pentenophenanthrene and its α- and β-methyl derivatives. The first paper disputes the claim of Diels and his collaborators (*Ber.*, 1927, **60**, 140; *Annalen*, 1930, **478**, 129) to have obtained chrysene by the dehydrogenation of cholesterol and cholic acid. All of the "chrysenähnliche" mixtures obtained by Ruzicka and his co-workers gave considerable depressions of melting point when mixed with authentic chrysene, and the same was true of the 2 : 7-dinitroanthraquinone complexes. The "chrysene-resembling" mixture which we obtained in a selenium dehydrogenation experiment with cholesterol (p. 1111) gave no depression of m. p. with chrysene. The formation of chrysene does not seem to us to present any difficulty in interpretation, for the temperature at which the dehydrogenation is effected is approaching that at which alkyl groups in the α-position to a condensed ring system become very labile (compare Cook, J., 1930, 1088; 1931, 490), so that if the five-membered ring of the sterol skeleton becomes ruptured at position 14 (sterol system of numbering), the subsequent conversion into chrysene would be relatively simple, particularly if the quaternary methyl group is in this position.

It is further asserted by Ruzicka *et al.* that the "$C_{25}H_{24}$" hydrocarbon from cholesterol cannot have the structure (A) assigned to it by Rosenheim and King (*Chem. and Ind.*, 1933, **52**, 301), as it is different from and not (as stated by Diels and Karstens) identical with the corresponding hydrocarbon obtained from ergosterol. We are unable to subscribe to this view. Apart from the crystallographic data which we are not competent to judge, we find the evidence of non-identity unconvincing, particularly as the higher aromatic hydrocarbons are very prone to form constant-melting mixtures with one another. Moreover, the chemical properties of the hydrocarbon from cholesterol are much more in accord with the fluorene structure suggested by Rosenheim and King. We have been quite unable to obtain any anthraquinone derivative by prolonged oxidation of the compound with excess of chromic acid in acetic acid, whereas such a derivative should be formed from a compound of the structure (B) advocated by Ruzicka. In any case, we have already commenced work on the synthesis of the compound having formula (A), and when this is complete, direct comparison will settle the question.

(A.)





(B.)

[R = C_4H_9 (from cholesterol) or C_5H_{11} (from ergosterol).]

Ruzicka's method of synthesis of 1 : 2-*cyclo*pentenophenanthrene is in some respects similar to our own. In fact, we had already contemplated it as one of several possible variations of our own synthesis. Contrary to his assertion, it is not new in principle; for instance, exactly analogous examples of cyclisation of keto-esters are cited by von Auwers and Möller (*J. pr. Chem.*, 1925, **109**, 124), *e.g.*, the conversion of ethyl α-oxalyl-γ-phenylbutyrate into ethyl 3 : 4-dihydronaphthalene-1 : 2-dicarboxylate. For the preparation of the parent hydrocarbon named in the title of the present communication, our method is much more convenient than that of Ruzicka.

Experimental.

The degree of unsaturation of ethylenic hydrocarbons and mixtures containing them was estimated by using the pyridine sulphate dibromide reagent of Rosenmund and Kuhnhenn (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154).

Some of the analyses (marked with an asterisk) were micro-analyses by Dr. A. Schoeller.

Derivatives of cyclo-*Olefins*.

1-*Phenylacetyl*-Δ^1-cyclo*hexene* (III).—To an ice-cold mixture of anhydrous stannic chloride (250 g.) and carbon disulphide (600 c.c.) was added slowly, with agitation, a mixture of phenylacetyl chloride (154 g.) and *cyclo*hexene (82 g.). After standing in an ice-bath for 4½ hours, the deep red solution was shaken with ice and hydrochloric acid, the carbon disulphide layer washed with water, dried (sodium sulphate), and treated with dimethylaniline (130 g.). After removal of the carbon disulphide, the residue was heated at 180° for 3 hours, dissolved in ether, and washed with dilute hydrochloric acid, dilute sodium carbonate (which removed 17 g. of phenylacetic acid) and finally with water. After removal of the ether, the dried solution was distilled in a vacuum. The first fraction (16 g.; b. p. 32—40°/5 mm.) was identified as *cyclo*hexyl chloride. The fraction, b. p. 158—161°/5 mm. (48 g.), set to a mass of crystals after several days (addition of light petroleum and cooling in ice-salt produced a further crop). These were twice recrystallised from methyl alcohol. The pure *ketone* (III) formed colourless needles, m. p. 46—48° (Found: C, 83·7; H, 8·0. $C_{14}H_{16}O$ requires C, 83·9; H, 8·0%) (semicarbazone, m. p. 168—169°). Titration with perbenzoic acid (Nametkin and Abakumovsky, *J. pr. Chem.*, 1927, **115**, 56) showed the presence of a double bond. This ketone was recovered unchanged after its pale yellow solution in concentrated sulphuric acid (1 : 3) had been kept at room temperature for 3 hours, and also after its benzene solution had been kept in contact with anhydrous aluminium chloride (1 mol.) for 24 hours at room temperature.

When treated with methylmagnesium iodide, 1-phenylacetyl-Δ^1-*cyclo*hexene formed an oil which did not crystallise. This was dehydrogenated with selenium at 280—300° for 24 hours, and yielded a liquid, b. p. 153—156°/12 mm., which did not crystallise when cooled in a freezing mixture, and gave no picrate; hence, 9-methylphenanthrene was not formed in this experiment.

Reduction of 1-phenylacetyl-Δ^1-*cyclo*hexene (3 g.) by means of amalgamated zinc (15 g.) and concentrated hydrochloric acid (30 c.c.) for 4 hours gave an oil, b. p. 153—159°/12—15 mm. (1·9 g.), which was heated with selenium (4 g.) at 340° for 24 hours, and the product extracted with benzene and distilled in a vacuum. The crystalline distillate was recrystallised from alcohol and shown to be phenanthrene (mixed m. p.; picrate, m. p. 143—144°).

1-α-*Naphthylacetyl*-2-*methyl*-Δ^1-cyclo*pentene* (IV).—1-Naphthylacetic acid was prepared by essentially the method of Mayer and Oppenheimer (*Ber.*, 1916, **49**, 2139), the bromination of 1-methylnaphthalene being carried out at 205—210°, and the product thrice distilled in a vacuum and then crystallised from light petroleum. The pure bromomethyl compound was converted into 1-naphthylacetic acid as described by Mayer and Oppenheimer. The acid (20 g.) was heated under reflux for 2 hours with thionyl chloride (80 c.c.), the excess of thionyl chloride removed in a vacuum, and the 1-naphthylacetyl chloride distilled (16 g.; b. p. 174°/15 mm.). According to D.R.-P. 230,237, this chloride undergoes internal condensation to acenaphthenone under the influence of aluminium chloride. No such condensation was effected by stannic chloride in carbon disulphide during 7 hours at room temperature.

A mixture of 1-naphthylacetyl chloride (13·8 g.) and 1-methyl-Δ^1-*cyclo*pentene (5·6 g.; Skraup and Binder, *Ber.*, 1929, **62**, 1135) was added, drop by drop, to an ice-cold mixture of anhydrous stannic chloride (18 g.) and carbon disulphide (40 c.c.). After standing in ice for 6½ hours, the mixture was worked up exactly as described for phenylacetyl*cyclo*hexene. The product, 5·8 g. of a pale yellow syrup, b. p. 190—205°/4—5 mm., was treated, in alcoholic solution, with picric acid (7 g.), and the *picrate* (6 g.), twice recrystallised from alcohol, formed canary-yellow needles, m. p. 130·5—131·5° (Found: C, 60·1; H, 4·4· N, 9·0*.

$C_{18}H_{18}O,C_6H_3O_7N_3$ requires C, 60·1; H, 4·4; N, 8·8%). 1-α-*Naphthylacetyl*-2-*methyl*-Δ¹-cyclo*pentene* (IV), obtained by shaking this picrate with ether and dilute sodium carbonate, and then distilling it in a vacuum, formed an almost colourless viscous oil which solidified on standing to a mass of crystals, m. p. 32—33° (Found: C, 86·2; H, 7·1. $C_{18}H_{18}O$ requires C, 86·4; H, 7·3%). This ketone, in which the presence of a double bond was shown by perbenzoic acid titration, gave a pale yellow solution in concentrated sulphuric acid, and yielded a semicarbazone, m. p. 253—254°.

When a similar condensation was attempted between 1-naphthylacetyl chloride and *cyclo*pentene no pure product could be isolated.

1-β-*Phenylethyl*-Δ¹-cyclo*hexene* (V).—A Grignard solution was prepared by gradual addition of a solution of β-phenylethyl chloride (77 g.) in anhydrous ether (500 c.c.) to magnesium turnings (13 g.) activated with iodine. A considerable amount of crystalline compound separated. After the magnesium had dissolved, the whole was cooled in ice and treated slowly, with agitation, with *cyclo*hexanone (49 g.). After 2 hours at room temperature, the product was treated with ice and ammonium chloride, the ethereal solution washed, dried (sodium sulphate), and the ether removed. The residual oil was distilled, and the fraction, b. p. 165°/10 mm., crystallised (49 g.). After two recrystallisations from light petroleum, 1-β-*phenylethyl*cyclo*hexanol* formed colourless needles, m. p. 55—56° (Found: C, 82·25; H, 9·7. $C_{14}H_{20}O$ requires C, 82·2; H, 9·9%). For dehydration, the recrystallised carbinol (17 g.) was heated at 160° for an hour with potassium hydrogen sulphate (25 g.). The resulting 1-β-*phenylethyl*-Δ¹-cyclo*hexene* (V; 14·5 g.) formed a colourless mobile liquid, b. p. 145°/10 mm., $d_4^{15°}$ 0·9587, $n_D^{19·7°}$ 1·5351, $[R_L]_D$ 60·43 (Calc., 60·58). The bromine absorption value agreed with one double bond (Found: C, 89·9; H, 9·8. $C_{14}H_{18}$ requires C, 90·2; H, 9·8%).

1-β-Phenylethyl-Δ¹-*cyclo*hexene was also formed when a solution of 1-β-phenylethyl*cyclo*hexanol (9·3 g.) in carbon disulphide (15 c.c.) was treated at 0° with anhydrous stannic chloride (6·5 c.c.) diluted with carbon disulphide (20 c.c.). After an hour the mixture was treated with ice and hydrochloric acid, and the olefin purified by distillation (b. p. 153—154°/15 mm., $n_D^{19·2°}$ 1·5388; 1 mol. bromine absorbed).

1-(β-1′-*Naphthylethyl*)-Δ¹-cyclo*pentene* (VIII).—(a) β-1-*Naphthylethyl alcohol*. This was prepared by Grignard (*Compt. rend.*, 1905, **141**, 45) from 1-naphthylmagnesium bromide and ethylene chlorohydrin. In these circumstances half of the Grignard reagent is converted into naphthalene and it was found better to use ethylene oxide. To an ice-cold Grignard solution, prepared from 1-bromonaphthalene (100 g.), magnesium turnings (12 g.), and anhydrous ether (500 c.c.), was slowly added a mixture of ethylene oxide (25 g.) and ether (50 c.c.). On then allowing the mixture to warm to room temperature, a vigorous reaction set in and was moderated, if necessary, by cooling. When the reaction had subsided, the ether was slowly removed on the water-bath, and the residue heated at 100° for an hour. It was then decomposed with ice and hydrochloric acid, extracted with ether, washed, dried, and fractionated in a vacuum. There were obtained 52 g. of β-1-naphthylethyl alcohol, b. p. 174—178°/13 mm., which rapidly crystallised on cooling.

(b) β-1-*Naphthylethyl chloride*. An ice-cold mixture of β-1-naphthylethyl alcohol (117 g.) and dimethylaniline (83 g.) was treated, drop by drop, with thionyl chloride (50 c.c.). After it had attained room temperature, the syrup was heated on the water-bath for ½ hour, diluted with water, extracted with ether, and washed with dilute hydrochloric acid, then dilute alkali, and finally water. The resulting β-1-*naphthylethyl chloride* (116 g.) formed a yellowish liquid, b. p. 167—168°/17 mm. (Found: C, 75·1; H, 5·75. $C_{12}H_{11}Cl$ requires C, 75·6; H, 5·8%). The *picrate* (from alcohol) formed orange needles, m. p. 67—68° (Found: C, 51·2; H, 4·8. $C_{12}H_{11}Cl,C_6H_3O_7N_3$ requires C, 51·5; H, 3·4%). (In the analysis of this and other picrates only the figures for carbon are significant. The high values for hydrogen are due to the fact that a copper spiral was not used to reduce oxides of nitrogen.)

(c) 1-(β-1′-*Naphthylethyl*)cyclo*pentanol* (VII). A Grignard solution, prepared from β-1-naphthylethyl chloride (114 g.), magnesium turnings (14·4 g.), and anhydrous ether (300 c.c.), was treated with *cyclo*pentanone (50·4 g.) exactly as described for the preparation of 1-β-phenylethyl*cyclo*hexanol. The crude carbinol was distilled in a vacuum, the lower-boiling fractions being rejected. The fraction, b. p. 197—198°/4—5 mm. (85 g.), crystallised on standing. For analysis, a sample of 1-(β-1′-*naphthylethyl*)cyclo*pentanol* (VII) was recrystallised 3 times from light petroleum, forming a colourless, micro-crystalline powder, m. p. 59·5—60° (Found: C, 85·0; H, 8·4. $C_{17}H_{20}O$ requires C, 84·9; H, 8·4%).

(d) *Dehydration of the carbinol* (VII). This was effected by heating the carbinol (80 g.) with potassium hydrogen sulphate (120 g.) at 160—170° for an hour, and yielded 68 g. of

1-(β-1′-*naphthylethyl*)-Δ¹-cyclo*pentene* (VIII), b. p. 198—202°/18 mm.; the *picrate*, prepared in alcoholic solution, formed orange-yellow needles, m. p. 78—79° (Found: C, 61·4; H, 5·2. $C_{17}H_{18},C_6H_3O_7N_3$ requires C, 61·2; H, 4·7%). This picrate was decomposed by shaking with ether and dilute sodium carbonate, and the pure olefin distilled in a vacuum over sodium. It formed a colourless mobile liquid, b. p. 164°/4—5 mm., $d_4^{20°}$ 1·0298, $n_D^{20°}$ 1·6034, $[R_L]_D$ 74·13 (Calc., 73·98) † (Found: C, 91·7; H, 8·1. $C_{17}H_{18}$ requires C, 91·8; H, 8·2%). Bromine absorption corresponded with one double bond.

Cyclisation Experiments.

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydrophenanthrene* (VI).—(a) 1-β-Phenylethyl*cyclo*hexanol (15 g.) was gradually added to concentrated sulphuric acid (10·5 c.c.) at −5°. After 1½ hours the mixture was allowed to warm to 0°, maintained at this temperature for ½ hour, and then poured on ice. The oil was extracted with ether, washed with alkali, dried, and twice distilled in a vacuum. The octahydrophenanthrene (2·9 g.), which absorbed no bromine, had b. p. 159°/15 mm. and $n_D^{19·2°}$ 1·5527 (Found: C, 90·0; H, 9·65. Calc.: C, 90·2; H, 9·8%). The poor yield was due to loss by sulphonation.

Dehydrogenation of this product with selenium at 320—340° gave phenanthrene, identified by direct comparison of the hydrocarbon and its picrate with authentic samples.

(b) When 1-β-phenylethyl*cyclo*hexanol (6·1 g.) was treated with stannic chloride in carbon disulphide under the conditions described above (p. 1107), and the mixture kept at 15° for 24 hours, 4·8 g. of hydrocarbon were formed, containing 60% of octahydrophenanthrene (estimated by bromine titration). The pure tricyclic hydrocarbon could be isolated from this mixture by washing its benzene solution with concentrated sulphuric acid. Selenium dehydrogenation of the mixture gave phenanthrene.

(c) Anhydrous aluminium chloride (4 g.) was added to a solution of 1-β-phenylethyl-Δ¹-*cyclo*hexene (V; 2·8 g.) in carbon disulphide (30 c.c.). After 24 hours the mixture was treated with ice and hydrochloric acid and yielded, after distillation, a liquid (1·6 g.) which contained 85% of the saturated isomeride.

(d) A solution of 1-β-phenylethyl-Δ¹-*cyclo*hexene (15 g.) in glacial acetic acid (135 c.c.) and concentrated sulphuric acid (15 c.c.) was boiled for an hour, diluted with water, extracted with benzene, washed free from acid, and distilled in a vacuum. The product (10 g.), which contained about 10% of olefin, was shaken in benzene solution with 85% sulphuric acid, and distilled over sodium; it was then shown to be completely saturated and had b. p. 164—166°/16 mm., $d_4^{15°}$ 1·0208, $n_D^{21°}$ 1·5688.

Derivatives of 1 : 2-cyclo*Pentenophenanthrene*.—(a) Finely-powdered anhydrous aluminium chloride (84 g.) was slowly added to an ice-cold solution of 1-(β-1′-naphthylethyl)-Δ¹-*cyclo*pentene (VIII; 70 g.) in carbon disulphide (700 c.c.). After being kept in the ice-chest for 24 hours, the clear dark red solution was poured off from the viscous mixture of resin and aluminium chloride, and shaken with ice and hydrochloric acid. The carbon disulphide was removed from the washed and dried solution on the water-bath, and the residual oil (58 g.) dissolved in alcohol and treated with picric acid (60 g.). The *picrate* of *trans*-1 : 2-*cyclo*pentano-1 : 2 : 3 : 4-tetrahydrophenanthrene (IX) was recrystallised from alcohol and then formed long vermilion needles, m. p. 128—129° (40 g.) (Found: C, 61·25; H, 5·0. $C_{17}H_{18},C_6H_3O_7N_3$ requires C, 61·2; H, 4·7%). It was shaken with ether and dilute sodium carbonate, and the hydrocarbon distilled in a vacuum over sodium. The viscous distillate (19 g.), which was saturated towards bromine, slowly solidified to a mass of long, colourless crystals, m. p. 35—36° (Found: C, 91·8; H, 8·2. $C_{17}H_{18}$ requires C, 91·8; H, 8·2%). trans-1 : 2-cyclo*Pentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IX) had b. p. 160—161°/3—4 mm., $d_4^{20°}$ 1·0859, $n_D^{20·2°}$ 1·6256, $[R_L]_D$ 71·99 (Calc., 72·25).

The alcoholic liquors from the above picrate were concentrated, and gave a further crystalline fraction of indefinite m. p. (90—110°). This was converted into the corresponding mixture of hydrocarbons (28 g.; denoted *cyclo*pentanotetrahydrophenanthrene, fraction 2). The final liquors were freed from picric acid, and the hydrocarbon mixture distilled (10 g.; *cyclo*pentanotetrahydrophenanthrene, fraction 3). Both fractions (2 and 3) were saturated towards bromine.

*cyclo*Pentanotetrahydrophenanthrene, fraction 3, was redistilled over sodium, and had b. p. 150—163°/3—4 mm., $d_4^{20°}$ 1·0708, $n_D^{20°}$ 1·6181 (Found: C, 90·8; H, 8·0. Calc. for $C_{17}H_{18}$: C, 91·8; H, 8·2%). This fraction gave no crystalline picrate in alcoholic solution.

† In computing this value and also that for the corresponding cyclic compound (below) an increment of 2·68 units has been added, this being the exaltation due to the naphthalene system as determined by Krollpfeiffer, *Annalen*, 1923, **430**, 202.

(b) An ice-cold solution of 1-(β-1′-naphthylethyl)*cyclo*pentanol (VII; 10 g.) in carbon disulphide (50 c.c.) was treated with anhydrous stannic chloride (5 c.c.). The whole was kept at room temperature for 24 hours, and the clear solution poured off from the red resin which had separated, and decomposed with water. The washed and dried carbon disulphide solution was freed from solvent and distilled in a vacuum (b. p. 163—173°/5—6 mm.). The bromine value indicated that this liquid contained 50% of unchanged olefin. Treatment with alcoholic picric acid gave a red picrate which, after recrystallisation from alcohol, had m. p. 127—128°, and was shown by mixed m. p. to be identical with the picrate described under (a).

(c) A mixture of 1-(β-1′-naphthylethyl)-Δ^1-*cyclo*pentene (VIII; 6 g.), glacial acetic acid (60 c.c.), and concentrated sulphuric acid (6 c.c.) was heated on the water-bath for ¾ hour. The cooled solution was diluted with water, extracted with ether, and the extract washed free from acid and distilled. The solid distillate, b. p. 215—235°/15 mm., was recrystallised from alcohol, the resulting 1 : 2-cyclo*pentenophenanthrene* (X) forming colourless needles, m. p. 134·5—135° [Found : C, 93·6; H, 6·5; *M**, (Rast), 207, 214. $C_{17}H_{14}$ requires C, 93·5; H, 6·5%; *M*, 218]. The *picrate*, prepared in alcoholic solution, formed bright orange needles, m. p. 134·5—135° (Found : N, 9·2*. $C_{17}H_{14},C_6H_3O_7N_3$ requires N, 9·4%). The m. p. of the hydrocarbon was unchanged after regeneration from the pure picrate.

(d) A solution of 1-(β-1′-naphthylethyl)*cyclo*pentanol (VII; 65 g.) in glacial acetic acid (585 c.c.) and concentrated sulphuric acid (65 c.c.) was heated on the water-bath for 1½ hours, during which the colour changed from red to deep blue, and sulphur dioxide was freely liberated. The hot solution was diluted with water until cloudy, cooled, and the resulting crystals collected, dissolved in xylene, the solution washed free from acid, the solvent removed, and the residue distilled in a vacuum (b. p. 200—240°/15 mm.). The crystalline distillate (35 g.) was recrystallised from alcohol and gave 20 g. of 1 : 2-*cyclo*pentenophenanthrene (m. p. 133·5—134·5°). Its *compound* with *s*.-trinitrobenzene separated from alcohol in soft, pale yellow needles, m. p. 166—167° (Found : C, 63·9; H, 4·0; N, 9·6*. $C_{17}H_{14},C_6H_3O_6N_3$ requires C, 64·0; H, 4·0; N, 9·7%). Addition of a solution of stannous chloride in hydrochloric acid to the boiling alcoholic solution of this compound gave the pure hydrocarbon, m. p. 135°.

1 : 2 : 3 : 4 : 10 : 11-*Hexahydrofluorene* (XV).—Attempts to effect cyclisation of 1-benzyl-Δ^1-*cyclo*hexene (XIV), prepared from 1-benzyl*cyclo*hexanol by dehydration with potassium hydrogen sulphate, were fruitless : stannic chloride in carbon disulphide gave the unchanged olefin (bromine absorption estimation) after 7 days at room temperature, and aluminium chloride in carbon disulphide at room temperature, or sulphuric acid in boiling glacial acetic acid, gave high-boiling resins. Hexahydrofluorene was obtained as follows : A mixture of 1-benzyl*cyclo*hexanol (20 g.) and phosphoric oxide (40 g.) was heated for 20 minutes at 140—150°. The product was extracted with benzene and distilled, giving 1 : 2 : 3 : 4 : 10 : 11-*hexahydrofluorene* (XV; 8 g.), which, after redistillation over sodium, formed a mobile liquid, saturated towards bromine, with an odour resembling that of *p*-cymene. It had b. p. 137°/15 mm., $d_4^{20°}$ 0·9880, $n_D^{20°}$ 1·5448 (Found : C, 90·5; H, 9·6. $C_{13}H_{16}$ requires C, 90·6; H, 9·4%).

Dehydrogenation of cyclo*Pentanotetrahydrophenanthrenes.*

In all the selenium dehydrogenation experiments the substance was heated in a Pyrex-glass flask in a metal-bath, the recorded temperatures being those of the bath.

(a) A mixture (5 g.) prepared by the action of stannic chloride on naphthylethyl*cyclo*pentanol as described under (b) (above) was heated with selenium (3·5 g.) at 305—315° for 20 hours. The product was extracted with ether and distilled over sodium. The distillate (3·1 g., b. p. 160—168°/3 mm.) formed a colourless viscous oil, and was treated with picric acid in alcoholic solution. The picrate, twice recrystallised from alcohol, formed long, vermilion needles, m. p. 128—129°, not depressed by the picrate of *trans*-1 : 2-*cyclo*pentano-1 : 2 : 3 : 4-tetrahydrophenanthrene.

The crystalline residue in the distillation flask was sublimed at 200—210°/3 mm., and the sublimate crystallised from alcohol, forming colourless leaflets (0·35 g.), m. p. 145—148° (Found : C, 93·6; H, 6·1. Calc. for $C_{17}H_{14}$: C, 93·5; H, 6·5%). This hydrocarbon, the m. p. of which was raised to 152—153° † by two recrystallisations from alcohol, was an impure specimen of 1 : 2-*cyclo*pentenophenanthrene. The pure hydrocarbon, m. p. 134—135°, could in no way be obtained by crystallisation alone, but was readily obtained by decomposition of the picrate (m. p. 133—134·5°) or the *s*-trinitrobenzene complex (m. p. 165·5—166·5°).

† In our preliminary communication this figure was erroneously given as the m. p. of 1 : 2-*cyclo*pentenophenanthrene. The correct figure (135°) had already been communicated to Dr. G. A. R. Kon (see this vol., p. 1083), and a specimen of the pure hydrocarbon sent to Dr. Rosenheim when the paper by Ruzicka and his collaborators appeared (p. 1105).

(b) The substance designated as *cyclo*pentanotetrahydrophenanthrene, fraction 3 (probably largely *cis*-isomeride; 5·5 g.), was heated with selenium (4 g.) at 310—325° for 17 hours. The crystalline product was extracted with alcohol, the extract boiled with charcoal, and concentrated. The crystals which separated (1·7 g.) were sublimed at 200°/3 mm., and the sublimate recrystallised from alcohol. The product formed colourless leaflets, m. p. 166—168° (0·85 g.). This also was an impure sample of 1 : 2-*cyclo*pentenophenanthrene, the pure hydrocarbon, m. p. 135°, being obtained by recrystallisation of the *s*-trinitrobenzene complex from benzene–methyl alcohol, followed by decomposition with stannous chloride.

(c) Selenium dehydrogenation of *cyclo*pentanotetrahydrophenanthrene, fraction 2, carried out as described under (b), gave essentially the same result. Here, however, the m. p. of the crystallised hydrocarbon (before conversion into the *s*-trinitrobenzene complex) was 172—174°.

(d) *trans*-1 : 2-*cyclo*Pentano-1 : 2 : 3 : 4-tetrahydrophenanthrene (IX) was recovered almost entirely unchanged after being heated with selenium at 310—320° for 24 hours. At 335—340° hydrogen selenide was freely liberated. If the reaction was stopped before completion, there was formed a mixture of unchanged material and the two indene compounds (probably XI and XII). The isolation of these was carried out as follows: The pure *trans*-tetrahydro-compound (IX; 3 g.) was heated with selenium (2·2 g.) at 330—340° for 24 hours. The filtered benzene extract was distilled after removal of the solvent on the water-bath. The distillate (1·6 g., b. p. 190—195°/3—4 mm.) was dissolved in hot alcohol and the solution allowed to crystallise. The crystals (0·6 g.) had m. p. 115—125° after sintering, and were treated with picric acid (0·7 g.) in boiling alcohol. The sparingly soluble picrate, recrystallised from benzene, had m. p. 192°. It was decomposed with boiling aqueous ammonia, and the hydrocarbon thrice recrystallised from alcohol (Found *: C, 94·15; H, 5·6. *M*, Rast, 194, 212. $C_{17}H_{12}$ requires C, 94·4; H, 5·6%; *M*, 216). 1 : 2-cyclo-$\Delta^{1':4'}$- (XI) or -$\Delta^{1':3'}$-*Pentadienophenanthrene* (XII) formed colourless rhombic plates, m. p. 142·5—143·5°. It gave an orange-red solution with a strong green fluorescence in concentrated sulphuric acid; on standing, the colour faded to yellow and the fluorescence became bluish-violet. The *picrate* separated from alcohol in long, ruby-red needles, m. p. 192—193° (Found *: C, 62·0; H, 3·5; N, 9·6. $C_{17}H_{12},C_6H_3O_7N_3$ requires C, 62·0; H, 3·4; N, 9·4%).

The original alcoholic liquors of the distilled dehydrogenation product were treated with picric acid (1 g.). The resulting picrate was recrystallised from benzene and then alcohol, and formed dark red needles, m. p. 208—209° (mixed m. p. with the picrate of m. p. 192°, 192—196°). The new picrate (0·2 g.) was then decomposed with sodium carbonate solution, and the product recrystallised from alcohol, in which it was readily soluble. This substance had m. p. 68—70°, and gave the same series of changes with concentrated sulphuric acid as the compound, m. p. 143°. There was insufficient material for further purification.

(e) A mixture of 1 : 2-*cyclo*pentenophenanthrene (X; 2·7 g.) and selenium (0·6 g.) was heated at 340° for 12 hours. The resulting solid was extracted with ether, the solvent removed, and the residue (1·6 g.) sublimed at 200—220°/4 mm. Crystallisation from alcohol then gave pure 1 : 2-*cyclo*pentenophenanthrene, m. p. 133—134° (identified by mixed m. p. and preparation of the picrate). Addition of picric acid to the alcoholic mother-liquors gave no indication of the presence of the indene compound (XI or XII).

Dehydrogenation of Cholesteryl Chloride.

(a) A mixture of cholesteryl chloride (27 g.) and selenium (9 g.) was slowly heated from 250° to 320° and then maintained at 320—340° for 72 hours, during which a further 19 g. of selenium were added in two portions. At this stage the product was extracted with benzene and distilled (15 g. of selenium recovered). The distillate, b. p. 180—260°/5—6 mm. (15 g.), was again treated with selenium (10 g.) at 320—340° for 48 hours, and the product extracted with ether and distilled (5·5 g. of selenium recovered). The fraction, b. p. 185—220°/4—5 mm. (4·5 g.), crystallised on cooling, and was dissolved in alcohol and treated with picric acid (4·5 g.). The picrate which separated was recrystallised from alcohol (2·3 g.; m. p. 110—113°), and then decomposed in ethereal solution with dilute sodium carbonate. The product was recrystallised from alcohol (0·65 g., m. p. 113—118°) and treated with *s*-trinitrobenzene (0·7 g.) in alcohol. The compound was recrystallised from benzene and then from alcohol (m. p. 148—149°) and decomposed by treatment with stannous chloride. After crystallisation from alcohol, the hydrocarbon formed colourless leaflets, m. p. 131—133° (sintering at 129°). The results of mixed m. p. determinations of this hydrocarbon and its derivatives with the corresponding compounds of 1 : 2-*cyclo*pentenophenanthrene are given in the table on p. 1103. Unlike the

pure synthetic compounds, neither the hydrocarbon from cholesterol nor its picrate consisted of well-formed crystals.

(b) In another experiment, 125 g. of cholesteryl chloride were heated with selenium (90 g. in all) at 330—350° for 144 hours, and the product fractionated at 12 mm. : (i) b. p. 210—265°; (ii) 265—285°; (iii) 285—320°. Fraction (i) was redistilled, and the lower-boiling fractions treated with picric acid. There was no difficulty in isolating the hydrocarbon, m. p. 122—124°, giving a picrate, m. p. 117—118° (compare Diels, Gädke, and Körding, *loc. cit.*). Various samples gave C, 92·3; 93·2; 92·3; H, 7·5, 6·9, 7·9%*. Fraction (iii) (11 g.) was diluted with ether (50 c.c.) and kept at 0° for 2 days, after which the crystals (0·5 g.) were collected. This substance was recrystallised thrice from benzene and once from acetic acid, and formed colourless leaflets, m. p. 221—222·5° (Found * : C, 92·9, 92·9; H, 7·3, 7·1. Calc. for $C_{25}H_{22}$: C, 93·1; H, 6·9%). The *molecular compound* with 2 : 7-dinitroanthraquinone was twice recrystallised from xylene and formed bright red needles, m. p. 239—240° (Found * : C, 75·7; H, 4·8. $C_{25}H_{22},C_{14}H_6O_6N_2$ requires C, 75·5; H, 4·55%).

(c) Another dehydrogenation of cholesteryl chloride was carried out nearly as in (a), except that the temperature was maintained at 340—360°, and on occasions rose to 370°. The fraction of distillate, b. p. 170—240°/4 mm., was subjected to picric acid treatment and the regenerated hydrocarbon crystallised from alcohol; it then had m. p. 143—148° (sintering at 130°). Further purification through the *s*-trinitrobenzene compound, followed by crystallisation of the regenerated hydrocarbon, gave a product which began to sinter at 210°, and melted at 230—233°. The mixed m. p. with chrysene (m. p. 248—249°) was 233—235°. This substance gave a compound with 2 : 7-dinitroanthraquinone, m. p. 270—273° (from xylene), the mixed m. p. with the analogous chrysene compound (m. p. 298—299°) being 274—284°. There was insufficient material for further purification.

4 : 5-*Benzhydrindene.*

4 : 5-*Benz*-3-*hydrindone* (XVI).—β-2-Naphthylpropionic acid was prepared by the method of Mayer and Sieglitz (*Ber.*, 1922, **55**, 1855). The m. p. of the intermediate β-2-naphthyl*iso*-succinic acid was 145°, and not 94—95° as stated by these authors. For conversion into the hydrindone, a mixture of β-2-naphthylpropionic acid (13 g.) and anhydrous stannic chloride (20 c.c.) was heated at 120° for 3 hours. The cooled mass was powdered, extracted with ether, the extract washed with sodium carbonate solution, and the solvent removed. The residue, after recrystallisation from aqueous acetic acid, gave 3·8 g. of 4 : 5-benz-3-hydrindone, m. p. 102—103°.

4 : 5-*Benzhydrindene* (XVII).—The foregoing ketone (10 g.) was reduced by boiling with concentrated hydrochloric acid (50 c.c.) and amalgamated zinc (30 g.) for 18 hours. The product was distilled in a vacuum, and the distillate (4·9 g.) purified through the picrate (orange needles, m. p. 109—110°; Kruber, *loc. cit.*, gives 110°). The regenerated hydrocarbon was distilled in a vacuum over sodium and had b. p. 170°/15 mm., $n_D^{19\cdot7°}$ 1·6323.

Summary.

(1) Convenient methods have been elaborated for the synthesis of condensed-ring compounds of hydrophenanthrene and hydrofluorene type by the cyclisation of aromatic compounds in which a cyclic system forms part of an unsaturated side chain.

(2) Comparison of a purified sample of the "$C_{18}H_{16}$" hydrocarbon obtained from cholesterol by selenium dehydrogenation with synthetic 1 : 2-*cyclo*pentenophenanthrene indicates that the cholesterol hydrocarbon consists of this compound contaminated with a very persistent impurity.

(3) The "$C_{25}H_{24}$" hydrocarbon from cholesterol has been further characterised and data are quoted in good agreement with the formula $C_{25}H_{22}$.

(4) The selenium dehydrogenation of condensed-ring hydrocarbons with a terminal five-membered ring has been studied, and the results suggest that the course pursued by the reaction is determined by the stereochemical configuration of the reduced ring system.

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