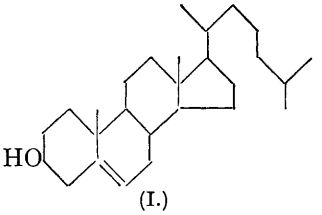
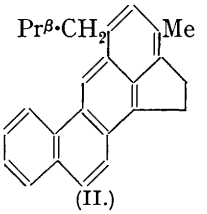
## 377. *The Synthesis of Compounds related to the Sterols, Bile Acids, and Oestrus-producing Hormones. Part IV. The Constitution of Diels's Hydrocarbon "* $C_{25}H_{24}$ *" from Cholesterol.*

By J. W. Cook, C. L. Hewett, W. V. Mayneord, and (Miss) E. Roe.

The only features of the structural formula for cholesterol (I) about which doubt is possible are the positions assigned to the two quaternary methyl groups. The hydrocarbon which Diels, Gädke, and Körding (*Annalen*, 1927, **459**, 1) first isolated as a lesser product of its selenium dehydrogenation may, from the various analytical data which have been recorded, be $C_{25}H_{22}$, $C_{25}H_{24}$, or $C_{26}H_{24}$. The last formula appears to be excluded by molecular-weight determinations made by measurements of density and unit cell dimensions of the crystals (private communication from Dr. J. D. Bernal and Miss D. Crowfoot). Hence both of the quaternary methyl groups must have been eliminated from the cholesterol molecule ($C_{27}H_{46}O$), and the formation of the hydrocarbon in question is most simply explained as due to cyclisation of the side chain during dehydrogenation with the production of an anthracene (II; $C_{25}H_{24}$) or a fluorene (III; $C_{25}H_{22}$) hydrocarbon.




(I.)

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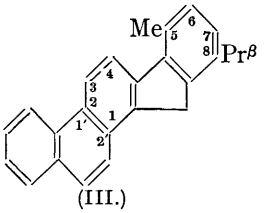
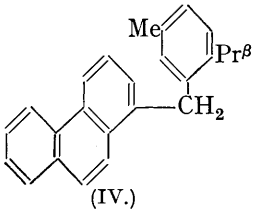



(III.)

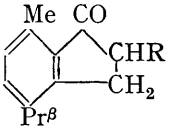
We have already given reasons why neither of these structures can be correct, in a recent note (*Chem. and Ind.*, 1934, **53**, 569) in which we stated that we had synthesised the fluorene hydrocarbon (III) and had made chemical and spectroscopic comparisons with the hydrocarbon from cholesterol. The present communication describes the details of our synthetic experiments and spectroscopic comparisons.

In Parts I and II (J., 1933, 1098; this vol., p. 365) it was shown that the cyclisation method by which several condensed ring systems were conveniently obtained proceeded with difficulty and gave poor yields when applied to the synthesis of hydrogenated fluorene systems. We have encountered the same hindrances during our attempts to synthesise the hydrocarbon (III), and the various devices to which we have had recourse in overcoming this obstacle have given very instructive results.

In the first synthesis which we attempted, 3-p-*cymylcarbinol*, obtained by passing formaldehyde into 3-*p*-cymylmagnesium bromide, was converted into its *chloride*, the magnesium derivative of which was condensed with 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene. The resulting resinous carbinol underwent simple dehydration without cyclisation when heated with phosphoric oxide, for the product was smoothly dehydrogenated by selenium to 1-(3′-p-*cymylmethyl*)*phenanthrene* (IV).




(IV.)

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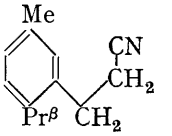
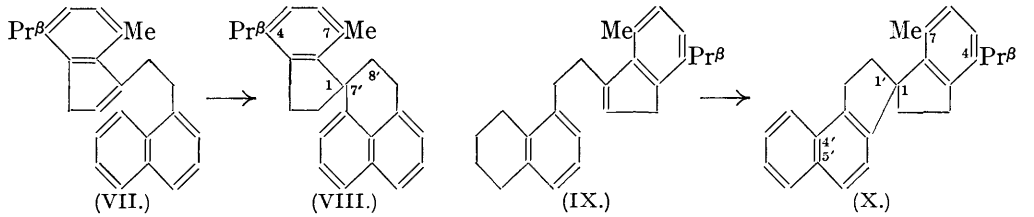



(VI.)

We then attempted to employ an adaptation of our method of synthesis of 1 : 2-*cyclo*pentenophenanthrene. For this purpose, 7-*methyl*-4-iso*propyl*-1-*hydrindone* (V; R = H) was required, and was obtained in good yield by stannic chloride dehydration of β-3-(p-*cymyl*)*propionic acid*, which resulted from the decarboxylation of the malonic acid arising

from the interaction of 3-chloromethyl-*p*-cymene with ethyl sodiomalonate. An alternative route to the above propionic acid was furnished by conversion of 3-bromo-*p*-cymene, by Grignard condensation with ethylene oxide, into β-3-(*p*-cymyl)ethyl alcohol, the bromide of which reacted with potassium cyanide to give β-3-(*p*-cymyl)propionitrile (VI). Owing to the poor yield obtained in the last stage, this method was abandoned in favour of the first method described.

When the hydrindone (V; R = H) was treated with β-1-naphthylethylmagnesium chloride there resulted a crystalline *carbinol*, which was dehydrated by potassium hydrogen sulphate to the *indene* (VII). Under various conditions of cyclisation this indene (or its antecedent carbinol) was converted into a saturated isomeric hydrocarbon which was unaffected by heating with selenium at 310—320°, and in the light of the observations recorded in Part II (*loc. cit.*) there can be little doubt that the cyclisation product is 7-*methyl*-4-iso*propylhydrindene*-1 : 7′-spiro-7′ : 8′-*dihydrophenalene* (VIII).

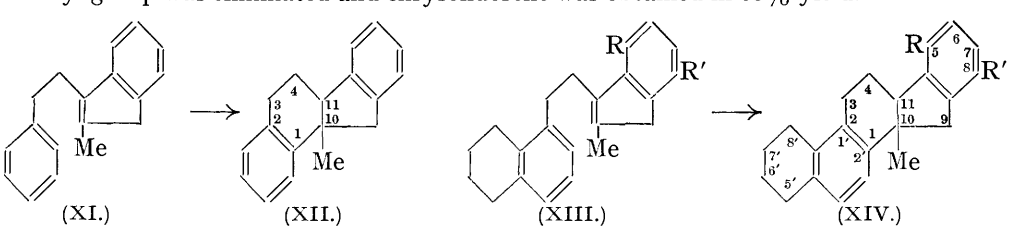



(VII.) (VIII.) (IX.) (X.)

To prevent this *peri*-ring closure in the naphthalene nucleus we next prepared the *tetrahydro*-derivative of (VII), represented by formula (IX). The β-5-*tetralylethyl alcohol* necessary for this purpose was readily obtained from ethylene oxide and the Grignard compound of the 5-bromotetralin of Smith (J., 1904, **85**, 729). The cyclisation product of (IX) could not be obtained crystalline, but was dehydrogenated by selenium to a *hydrocarbon* (isolated as the *picrate*) isomeric with, but different from, the spiran (VIII). To this new hydrocarbon we attribute formula (X). Traces of a high-melting crystalline product were formed simultaneously, but (X) was the essential product of the reactions.

The results of these cyclisation experiments are in complete harmony with the conclusions formulated in Part II, and the problem was therefore to effect cyclisation of compounds of the type (VII) or (IX) in such manner as to diminish or prevent spiran-formation. Our experience has shown that the course of the cyclisation is in no way modified by the nature of the cyclising agent or experimental conditions, but rather by the molecular circumstances of the compound. It was shown in Part III (Cohen, Cook, Hewett, and Girard, this vol., p. 653) that the attachment of a methyl group to the second carbon atom of the ethylenic linkage was a very effective device for avoiding spiran formation, and we therefore resolved to test its efficacy with the type of compound at present under review.

Although we had already synthesised chrysofluorene (1 : 2-benzfluorene) by cyclisation of 3-β-phenylethylindene and dehydrogenation of the product (Part II, *loc. cit.*), the yields were poor in both operations and it is now evident that the liquid which we regarded as tetrahydrochrysofluorene was a mixture of this hydrocarbon with the isomeric spiran. 3-β-*Phenylethyl*-2-*methylindene* (XI) has now been obtained in 80% yield from 2-methyl-1-hydrindone and β-phenylethylmagnesium chloride; it was rapidly converted by aluminium chloride in carbon disulphide at 0° into the isomeric *methyltetrahydrochrysofluorene* (XII), which was isolated in 82% yield. On dehydrogenation with selenium the quaternary methyl group was eliminated and chrysofluorene was obtained in 65% yield.

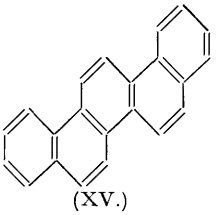


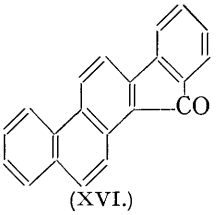

(XI.) (XII.) (XIII.) (XIV.)

These reactions furnish a convenient and simple synthesis of chrysofluorene, the yield being 40% with reference to the methylhydrindone. This indicates the remarkable influence of the methyl group in promoting ring closure in the sense (XI) ⟶ (XII), for when the methyl group was absent the yield of chrysofluorene was only 1·2% with respect to the hydrindone employed. It is also noteworthy that all of the Grignard condensations which we have carried out with hydrindone derivatives in which a methyl group is at position 2 have given uniformly high yields, doubtless because aldol condensations are impossible with this type of hydrindone.

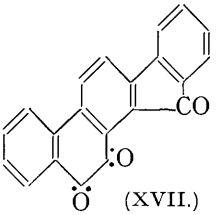
This synthesis of chrysofluorene has been extended, with equally satisfactory results, to 2′ : 1′-*naphtha*-1 : 2-*fluorene* and its 5-methyl-8-*iso*propyl derivative (III). In the former case β-5-tetralylethylmagnesium chloride was condensed with 2-methyl-1-hydrindone to give the *indene* (XIII; R = R′ = H), which was readily transformed into the crystalline pentacyclic *hydrocarbon* (XIV; R = R′ = H); this was converted by selenium dehydrogenation into 2′ : 1′-naphtha-1 : 2-fluorene. The analogous *methyliso*propyl compounds (XIII and XIV; R = Me, R′ = $Pr^{\beta}$) were obtained in precisely the same manner from 2 : 7-*dimethyl*-4-iso*propyl*-1-*hydrindone* (V; R = Me), which was prepared in excellent yield by a suitable modification of the method used for the synthesis of 7-methyl-4-*iso*propyl-1-hydrindone (V; R = H).

In some respects 2′ : 1′-naphtha-1 : 2-fluorene resembles picene (XV), which has a similar molecular structure. For example, like picene, naphthafluorene is a very high-melting, sparingly soluble compound which crystallises in colourless plates, and its m. p. (328°) is not depressed by admixture with picene (m. p. 354°). On oxidation, 2′ : 1′-naphtha-1 : 2-fluorene was converted first into 2′ : 1′-*naphtha*-1 : 2-*fluorenone* (XVI) and then into the *ketoquinone* (XVII).


(XV.)



(XVI.)



(XVII.)

In Part I it was suggested that the explanation of the discrepancy between the statement of Diels and Karstens (*Annalen*, 1930, **478**, 129) that chrysene was the chief product of selenium dehydrogenation of cholic acid, and the observations of Ruzicka and his collaborators (*Helv. Chim. Acta*, 1933, **16**, 224, 812), who were unable to isolate chrysene, was due to the use of higher temperatures by Diels and Karstens. This suggestion has been amply confirmed by more recent work of Ruzicka, Thomann, Brandenberger, Furter, and Goldberg (*ibid.*, 1934, **17**, 200), who showed that both chrysene and picene are formed by rearrangement of the bile-acid ring system when the dehydrogenation is effected at high temperatures (chrysene notably at 420°). It therefore seemed of interest to examine the high-temperature dehydrogenation of our methyloctahydronaphthafluorene (XIV; R = R′ = H), which might conceivably rearrange to give picene (XV). Dehydrogenation occurred exceedingly rapidly at 400—420°; however, the only pure compound isolated was naphthafluorene (identified by oxidation), but we are not prepared to assert that no trace of picene was formed, as the detection of a small amount of picene mixed with naphthafluorene would present considerable difficulty.

5-*Methyl*-8-iso*propyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene* (III) was not identical with the Diels hydrocarbon " $C_{25}H_{24}$ " from cholesterol, but was oxidised to a *ketone* which, like 2′ : 1′-naphtha-1 : 2-fluorenone and also the ketone formed by oxidation of the Diels hydrocarbon, gave an intense purple solution in concentrated sulphuric acid, the colour afterwards fading to magenta.

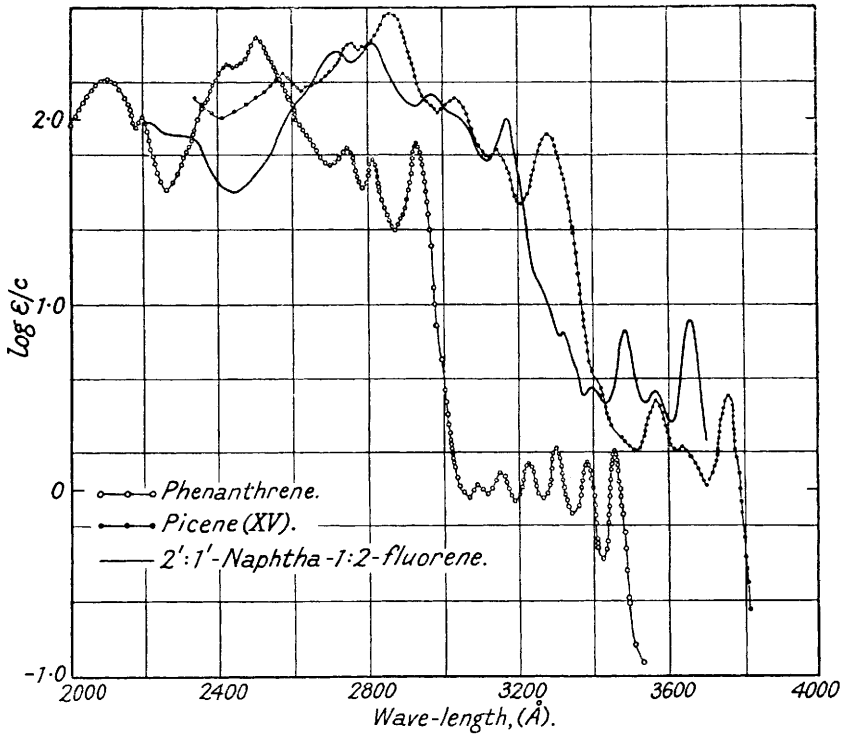
Another point of similarity between the Diels hydrocarbon and the synthetic naphthafluorene hydrocarbons was found in their photosensitivity. Their solutions all become intensely yellow on brief exposure to strong light, and in the case of methyl*iso*propyl-

naphthafluorene this tendency was so marked that the isolation of the colourless crystalline hydrocarbon was very troublesome.

*Ultra-violet Absorption Spectra.*

*Technique.*—A Hilger medium quartz spectrograph was employed. For the qualitative determination of the general form of the absorption curve a hydrogen discharge tube was used as the source of light. The continuous hydrogen spectrum facilitates the detection of very fine bands which might otherwise be overlooked. For quantitative measurements a Spekker photometer was attached to the Hilger spectrograph, and a condensed spark between tungsten-steel electrodes used as a source of light. A micrometer Baly tube,

FIG. 1.



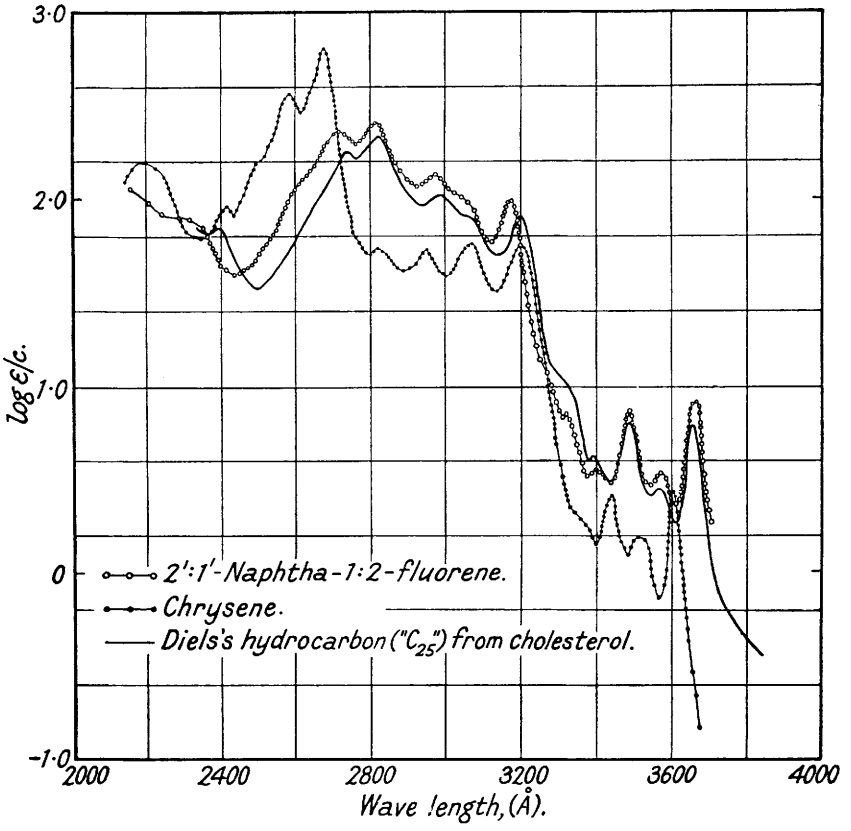

in which the length is continuously variable from 0 to 5 mm., was used as the absorption cell, and for the less soluble compounds 10 mm. and 100 mm. cells were used in addition. The measurements were made with alcoholic solutions of all of the compounds except picene, which is too sparingly soluble in alcohol, so that chloroform solutions were employed. However, a preliminary survey of picene in alcohol, using the hydrogen discharge tube, showed that all the peaks observed in chloroform solution were reproduced, but were 20—30 Å. nearer to the ultra-violet end of the spectrum. For comparison of the effects of these two solvents the curves of 2′ : 1′-naphtha-1 : 2-fluorene were accurately determined in both chloroform and alcohol. The results are given in the appropriate table.

*Preparation of Reference Substances.*—For comparison with the naphthafluorene hydrocarbons, pure synthetic specimens of the following hydrocarbons were prepared: Phenanthrene was obtained by selenium dehydrogenation of 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene and purified through its picrate. Chrysene was prepared by the method of Cook and Hewett (this vol., p. 372), and picene was obtained from dinaphthylethane by the method of Ruzicka and Hösli (*Helv. Chim. Acta*, 1934, **17**, 470). For the preparation of the Diels hydrocarbon " $C_{25}H_{24}$," cholesterol was dehydrogenated with selenium; the crystalline

material isolated from the appropriate fraction was repeatedly crystallised from pyridine. It formed colourless leaflets, m. p. 225—226° (corr.), in agreement with Ruzicka, Goldberg, and Thomann (*ibid.*, 1933, **16**, 827).

*Results.*—2′ : 1′-Naphtha-1 : 2-fluorene and picene are both related to 2-phenylphenanthrene. As might be expected, conjugation of the phenyl group with the phenanthrene system is attended by marked modification of the ultra-violet absorption bands of phenanthrene. This is particularly the case with the group of six bands in the phenanthrene spectrum at 3000—3500 Å. (Fig. 1). Naphthafluorene, in which the phenyl group and the phenanthrene system are united at second points of attachment through a saturated methylene group, shows less modification of these bands (five of them can still be detected) than picene, where the phenyl group and the phenanthrene system are linked a second time

FIG. 2.



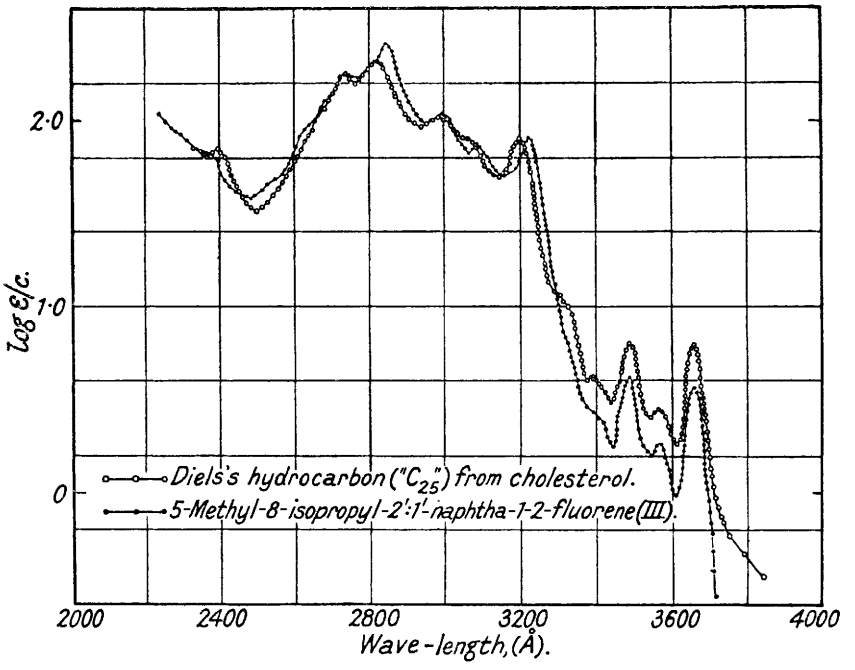

through two ethylenic carbon atoms. In picene, only three of the bands of this group survive.

Comparison of the curves of chrysene, naphthafluorene, and the Diels hydrocarbon "$C_{25}H_{24}$" (Fig. 2) shows that the curve of the Diels hydrocarbon closely resembles that of naphthafluorene, but is widely different from that of chrysene. Each band of naphthafluorene is reproduced in the spectrum of the Diels hydrocarbon, with very little difference in the wave-lengths of the maxima. The intensities of the bands of naphthafluorene are in general greater than those of the Diels hydrocarbon. This would agree with the conception that the latter is an alkyl derivative of naphthafluorene.

Fig. 3 shows that the curves of 5-methyl-8-*iso*propyl-2′ : 1′-naphtha-1 : 2-fluorene and the Diels hydrocarbon also resemble one another closely, although there are significant

differences in the wave-lengths of the maxima in the region 2700—3300 Å., and in the extinction coefficients in the region 3300—3800 Å.

FIG. 3.




*Tables of wave-lengths of maxima and minima, with extinction coefficients.*

$\lambda$ = wave-length in Å.; $\epsilon = \log \frac{I_0}{I} / l$; $c$ = concentration (g. per litre).

*Phenanthrene.*

| Maxima. | | Minima. | |
|---|---|---|---|
| λ. | log ε/c. | λ. | log ε/c. |
| 3458 | 0·210 | 3425 | −0·377 |
| 3382 | 0·152 | 3345 | −0·131 |
| 3300 | 0·223 | 3265 | −0·046 |
| 3228 | 0·146 | 3189 | −0·061 |
| 3154 | 0·093 | 3113 | −0·022 |
| 3090 | 0·021 | 3067 | −0·041 |
| 2929 | 1·860 | 2870 | 1·398 |
| 2812 | 1·763 | 2785 | 1·613 |
| 2746 | 1·839 | 2699 | 1·740 |
| 2507 | 2·428 | 2434 | 2·270 |
| 2425 | 2·290 | 2260 | 1·602 |
| 2196 | 2·006 | 2177 | 1·942 |
| 2101 | 2·204 | | |

*Chrysene.*

| Maxima. | | Minima. | |
|---|---|---|---|
| λ. | log ε/c. | λ. | log ε/c. |
| 3604 | 0·431 | 3566 | −0·143 |
| 3513 | 0·176 | 3481 | 0·093 |
| 3440 | 0·418 | 3399 | 0·149 |
| 3197 | 1·748 | 3131 | 1·494 |
| 3063 | 1·752 | 2998 | 1·580 |
| 2947 | 1·716 | 2881 | 1·613 |
| 2816 | 1·721 | 2790 | 1·699 |
| 2675 | 2·797 | 2610 | 1·455 |
| 2580 | 2·544 | 2433 | 1·907 |
| 2415 | 1·945 | 2341 | 1·777 |
| 2195 | 2·184 | | |

*Picene* (in chloroform).

| Maxima. | | Minima. | |
|---|---|---|---|
| 3765 | 0·512 | 3704 | 0·033 |
| 3641 | 0·236 | 3628 | 0·223 |
| 3573 | 0·500 | 3521 | 0·212 |
| 3283 | 1·914 | 3205 | 1·542 |
| 3148 | 1·825 | 3123 | 1·785 |
| 3038 | 2·101 | 2987 | 2·037 |
| 2865 | 2·572 | 2778 | 2·371 |
| 2755 | 2·398 | 2621 | 2·155 |
| 2575 | 2·250 | 2410 | 2·0 |

*Diels's Hydrocarbon* "$C_{25}H_{24}$."

| Maxima. | | Minima. | |
|---|---|---|---|
| 3654 | 0·797 | 3610 | 0·260 |
| 3562 | 0·447 | 3541 | 0·415 |
| 3485 | 0·806 | 3438 | 0·477 |
| 3390 | 0·622 | 3375 | 0·608 |
| 3198 | 1·910 | 3138 | 1·696 |
| 2980 | 2·009 | 2934 | 1·960 |
| 2822 | 2·328 | 2760 | 2·218 |
| 2730 | 2·243 | 2492 | 1·519 |
| 2393 | 1·845 | 2366 | 1·813 |

5-*Methyl*-8-iso*propyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene*.

| Maxima. | | Minima. | |
|---|---|---|---|
| λ. | log ε/*c*. | λ. | log ε/*c*. |
| 3660 | 0·544 | 3610 | −0·046 |
| 3564 | 0·230 | 3545 | 0·176 |
| 3484 | 0·591 | 3443 | 0·204 |
| 3218 | 1·892 | 3140 | 1·699 |
| 3079 | 1·860 | 3059 | 1·820 |
| 2983 | 2·021 | 2943 | 1·972 |
| 2840 | 2·398 | 2758 | 2·199 |
| 2729 | 2·225 | 2478 | 1·580 |

2′ : 1′-*Naphtha*-1 : 2-*fluorene* (in alcohol) (Figs. 1 and 2).

| Maxima. | | Minima. | |
|---|---|---|---|
| λ. | log ε/*c*. | λ. | log ε/*c*. |
| 3657 | 0·919 | 3603 | 0·362 |
| 3567 | 0·532 | 3538 | 0·470 |
| 3480 | 0·860 | 3434 | 0·477 |
| 3393 | 0·544 | 3372 | 0·515 |
| 3314 | 0·845 | 3308 | 0·833 |
| 3168 | 2·0 | 3115 | 1·778 |
| 2968 | 2·134 | 2921 | 2·068 |
| 2810 | 2·407 | 2758 | 2·301 |
| 2715 | 2·367 | 2442 | 1·602 |

2′ : 1′-*Naphtha*-1 : 2-*fluorene* (in chloroform).

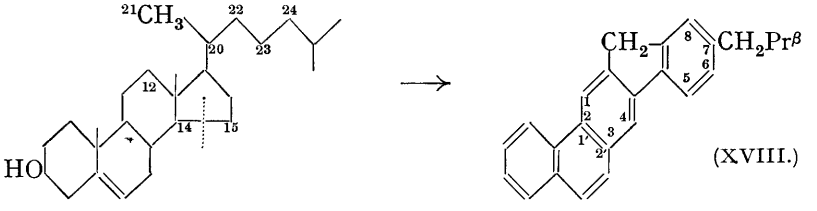
| Maxima. | | Minima. | |
|---|---|---|---|
| λ. | log ε/*c*. | λ. | log ε/*c*. |
| 3662 | 0·898 | 3621 | 0·204 |
| 3573 | 0·453 | 3550 | 0·398 |
| 3495 | 0·884 | 3445 | 0·438 |
| 3410 | 0·498 | 3385 | 0·458 |
| 3329 | 0·767 | 3307 | 0·744 |
| 3193 | 1·973 | 3140 | 0·754 |
| 3085 | 1·987 | 3074 | 1·973 |
| 2995 | 2·173 | 2943 | 2·079 |
| 2844 | 2·371 | 2783 | 2·248 |
| 2750 | 2·279 | 2475 | 1·560 |

## Discussion.

From the foregoing chemical and spectroscopic comparisons it is clear that the Diels hydrocarbon " $C_{25}H_{24}$ " from cholesterol is closely related to naphthafluorene, and since the Diels hydrocarbon is not represented by structure (III) it is apparent that the ring closure which occurs during dehydrogenation is attended by either group migration or rearrangement to one of the five other non-anthracenoid naphthafluorene ring systems which are theoretically possible. A crystallographic comparison of our synthetic 5-methyl-8-*iso*propyl-2′ : 1′-naphtha-1 : 2-fluorene with the Diels hydrocarbon has now been made by Dr. Bernal and Miss Crowfoot; they will publish their results shortly, but in the meantime they report that the probable molecular length, calculated from the dimensions of the unit cell, of the Diels hydrocarbon is appreciably greater than that of methyl*iso*propylnaphthafluorene; comparable, in fact, with that of cholesterol.

Reference to models shows that on the assumption that the cholesterol side chain becomes linked to the five-membered ring to give the 2′ : 1′-naphtha-1 : 2-fluorene ring system, the greatest molecular length can be attained by migration of the *iso*propyl group from position 8 to the adjacent position 7. This is a possibility which must be borne in mind, but it is difficult to understand why this migration should occur during the dehydrogenation of cholesterol, although it might well happen in the case of ergosterol and phytosterols (compare Cook, *Chem. and Ind.*, 1934, **53**, 311).

A better explanation has been suggested by Dr. Bernal (private communication). The essence of this is that the five-membered ring which finally appears in the aromatic hydrocarbon is not the one which was originally present in the cholesterol molecule. The changes which are postulated are (i) fission of the five-membered ring between $C_{14}$ and $C_{15}$, as indicated by the dotted line, (ii) linking of $C_{15}$ with $C_{23}$ of the side chain, and (iii) formation of a new five-membered ring by the methyl group ($C_{21}$) of the side chain becoming attached to $C_{12}$.* The final product would thus be 7-*iso*butyl-1′ : 2′-naphtha-2 : 3-fluorene (XVIII) :




(XVIII.)

All the facts can be reconciled with this structure for the Diels hydrocarbon from cholesterol. A model shows an appreciably longer molecule than that representing structure (III). Both naphthafluorene ring systems (III and XVIII) are derived from 2-phenylphenanthrene, differing only in the point of attachment of the saturated methylene group, and the ultraviolet absorption properties would clearly be similar. The presence of one substituent only in (XVIII) is consistent with the fact that the extinction coefficients of the bands of the

* The alternative attachment of $C_{21}$ to $C_{14}$ would lead to the formulation as 2′ : 1′-naphtha-1 : 2-fluorene (m. p. 328°) for the analogous hydrocarbon (m. p. 275°) obtained from cholic acid by Ruzicka (*Helv. Chim. Acta*, 1933, **16**, 216; 1934, **17**, 200).

Diels hydrocarbon in the region 3300—3800 Å. are slightly greater than those of (III) (Fig. 3). Above all, the suggested mechanism requires that the corresponding hydrocarbons from cholesterol, ergosterol, and sitosterol or stigmasterol should be different from one another (an additional alkyl group is attached to $C_{24}$ of the side chain). That they are different, although very similar, has been strikingly demonstrated by Ruzicka and his collaborators (*Helv. Chim. Acta*, **1934**, **17**, 200).

We are now engaged in the synthesis of the hydrocarbon represented by formula (XVIII) as well as the parent hydrocarbon containing this ring system.

We would lay final emphasis on two points. (1) The products of dehydrogenation of sterols and bile acids which are formed by molecular rearrangements (chrysene, picene, and the pentacyclic hydrocarbons of the type discussed in the present communication) arise only as minor products and are the results of the special susceptibility of the sterol molecule to undergo rearrangement. This is conditioned by the terminal five-membered ring with its labile side chain. Such rearrangements have not yet been observed among simpler polycyclic hydroaromatic compounds, which are normally converted smoothly in good yield into the corresponding aromatic compounds. (2) We would point out that the rearrangements which occur are determined mainly by the high temperatures which must be used for dehydrogenation, and are not specially attributable to the influence of selenium. There are several observations which justify this conclusion; for example, the fact that the hydrocarbon " $C_{25}H_{24}$ " from cholesterol is obtained by dehydrogenation with palladium as well as with selenium (Ruzicka, Goldberg, and Thomann, *loc. cit.*).

## Experimental.

* Denotes microanalyses by Dr. A. Schoeller (Berlin).
† Denotes microanalyses by Dr. G. Weiler (Oxford).

### 1-(3′-p-*Cymylmethyl*)*phenanthrene* (IV).

3-*Chloromethyl*-p-*cymene*.—3-Bromo-*p*-cymene was prepared from thymol and phosphorus pentabromide (Fileti and Crosa, *Gazzetta*, **1886**, **16**, 291). Interaction of 3-*p*-cymylmagnesium bromide with unimolecular formaldehyde (compare Ziegler, *Ber.*, **1921**, **54**, 737; Ziegler and Tiemann, *ibid.*, **1922**, **55**, 3406) gave somewhat varying yields, the best being about 40%. The following is a description of a representative experiment: 3-Bromo-*p*-cymene (106 g.), diluted with anhydrous ether (350 c.c.), was gradually added to magnesium turnings (12 g.) activated with iodine. The whole was then boiled for 2 hours, but much magnesium remained undissolved. Formaldehyde, obtained by heating dry trioxymethylene (35 g.), was passed into the ice-cold solution; the whole was kept over-night at room temperature, decomposed with ice and hydrochloric acid, and the product isolated from the ethereal solution and twice distilled in a vacuum. 3-*p*-Cymylcarbinol formed a yellowish, somewhat viscous liquid (27 g.), b. p. 143—144°/25 mm., which was not obtained analytically pure (Found: C, 77·8; H, 9·3. Calc.: C, 80·4; H, 9·8%). Its 3 : 5-*dinitrobenzoate* crystallised from alcohol in colourless fibrous needles, m. p. 85—86° (†Found: C, 60·35; H, 5·0. $C_{18}H_{18}O_6N_2$ requires C, 60·3; H, 5·1%).

Thionyl chloride (47 g.) was added dropwise to an ice-cold mixture of 3-*p*-cymylcarbinol (60 g.) and dimethylaniline (47 g.). The whole was then heated on the water-bath until evolution of sulphur dioxide ceased, and was then cooled, diluted with water, extracted with ether, and the extract washed and distilled. 3-*Chloromethyl*-p-*cymene* (52 g.) was redistilled, forming a yellowish mobile liquid, b. p. 129—130°/25 mm. (Found: C, 72·4; H, 8·15. $C_{11}H_{15}Cl$ requires C, 72·3; H, 8·3%).

1-(3′-p-*Cymylmethyl*)*phenanthrene* (IV).—To an ice-cold Grignard solution prepared from 3-chloromethyl-*p*-cymene (10 g.), magnesium turnings (1·4 g.), and anhydrous ether (50 c.c.) was added a solution of 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (10·5 g.) in anhydrous ether (140 c.c.). After 2 hours at room temperature the whole was decomposed with water and ammonium chloride, the ethereal solution washed and dried, and the ether removed. The resulting syrup (17·5 g.) gave no crystalline material and was heated with phosphoric oxide (35 g.) at 145—150° for ½ hour. The highest fraction, b. p. 260—270°/4—5 mm., formed a viscous resin (3·8 g.), which gave no crystalline picrate. It was heated with selenium (3·5 g.) at 320—340° for 19 hours, and the product distilled. The distillate, b. p. 250°/3—4 mm., was dissolved in a little ether, and the solution cooled in a freezing mixture. The resulting crystals (0·9 g.) were recrystallised from acetic acid and then alcohol. 1-(3′-p-*Cymylmethyl*)*phen-*

*anthrene* (IV) formed colourless needles, m. p. 115—116° (*Found : C, 92·6; H, 7·4; *M*, Rast method, 292, 300. $C_{25}H_{24}$ requires C, 92·5; H, 7·5%; *M*, 324). The s.-*trinitrobenzene complex* of this hydrocarbon crystallised from alcohol in small canary-yellow needles, m. p. 134—135° (*Found : C, 69·2; H, 5·1; N, 7·7. $C_{25}H_{24},C_6H_3O_6N_3$ requires C, 69·2; H, 5·1; N, 7·8%). The hydrocarbon regenerated by reduction with stannous chloride had the m. p. given above.

1-3′-*Methyl*-6′-iso*propylbenzoylphenanthraquinone*.—A solution of the hydrocarbon (IV) (0·2 g.) and sodium dichromate (0·6 g.) in purified acetic acid (5 c.c.) was heated on the water-bath for 4½ hours. The cooled solution was diluted with water, and the precipitate collected and dissolved in alcohol. After a time the solution crystallised; the crystals were twice recrystallised from benzene, forming small orange-brown needles, m. p. 208—209° (*Found : C, 81·4; H, 5·4. $C_{25}H_{20}O_3$ requires C, 81·5; H, 5·5%). The yield of the pure quinone was small. When warmed with *o*-phenylenediamine in acetic acid, it gave almost colourless needles, m. p. 187°, the amount of which was too small for purification.

*Formation of Spirans* (VIII *and* X).

β-3-(p-*Cymyl*)*propionic Acid*.—A solution of ethyl malonate (96 g.) in pure benzene (110 c.c.) was heated on the water-bath with sodium wire (6·7 g.). After all the sodium had dissolved, 3-chloromethyl-*p*-cymene (50 g.) was added. The whole was boiled for 2 hours, kept at room temperature over-night, and then diluted with water. The washed benzene solution was dried and distilled. The ester (b. p. 195—200°/14 mm.; 68 g.) was heated on the water-bath for ½ hour with methyl alcohol (100 c.c.) and 50% aqueous potassium hydroxide (85 c.c.). After dilution with water and extraction with ether, the aqueous solution was acidified and the crude malonic acid derivative extracted with ether. For decarboxylation, this was heated at 180° for ½ hour, and then distilled. The crystalline distillate, b. p. 195°/11 mm., of β-3-(p-*cymyl*)*propionic acid* (38 g.) was sufficiently pure for the next stage. For analysis, a sample was recrystallised from light petroleum, forming colourless crystals, m. p. 61—61·5° (Found : C, 75·55; H, 8·7. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%).

7-*Methyl*-4-iso*propyl*-1-*hydrindone* (V; R = H).—The foregoing acid was heated with an equal weight of anhydrous stannic chloride at 120° for an hour. The product was cooled, treated with dilute hydrochloric acid, and extracted with ether. Nearly half of the original acid was recovered from the extract by shaking with dilute alkali. The ether was then removed, and the residue distilled. 7-*Methyl*-4-iso*propyl*-1-*hydrindone*, b. p. 165—167°/15 mm., was obtained in 90% yield with reference to the amount of acid actually converted. A pure sample, recrystallised from light petroleum, formed colourless needles, m. p. 46—48° (Found : C, 82·8; H, 8·3. $C_{13}H_{16}O$ requires C, 82·9; H, 8·5%). This ketone gave a phenylhydrazone, m. p. 96—97°.

1-*Hydroxy*-1-(β-1′-*naphthylethyl*)-7-*methyl*-4-iso*propylhydrindene*.—To an ice-cold Grignard solution prepared from β-1-naphthylethyl chloride (31·6 g.), magnesium turnings (4 g.), and anhydrous ether (100 c.c.) was added a solution of 7-methyl-4-*iso*propyl-1-hydrindone (20 g.) in ether (50 c.c.). After 2 hours at room temperature the product was treated with ice and ammonium chloride, and the ethereal solution washed, dried (sodium sulphate), and the ether removed on the water-bath. A solution of the residual oil in light petroleum deposited colourless crystals (16 g.) of 1-*hydroxy*-1-(β-1′-*naphthylethyl*)-7-*methyl*-4-iso*propylhydrindene*. This carbinol separated from methyl alcohol as a colourless crystalline powder, m. p. 115·5—116° (Found : C, 87·2; H, 8·1. $C_{25}H_{28}O$ requires C, 87·1; H, 8·2%).

3-(β-1′-*Naphthylethyl*)-4-*methyl*-7-iso*propylindene* (VII).—This was formed when the above carbinol (5 g.) was heated at 160° for an hour with potassium hydrogen sulphate (7·5 g.). The *indene* was isolated, and recrystallised from alcohol, forming colourless leaflets, m. p. 92—93° (Found : C, 92·1; H, 7·9. $C_{25}H_{26}$ requires C, 92·0; H, 8·0%). No rearrangement of the ethylenic bond occurred under the influence of boiling 10% methyl-alcoholic potassium hydroxide.

7-*Methyl*-4-iso*propylhydrindene*-1 : 7′-spiro-7′ : 8′-*dihydrophenalene* (VIII).—(a) A mixture of 1-hydroxy-1-(β-1′-naphthylethyl)-7-methyl-4-*iso*propylhydrindene (15 g.), acetic acid (135 c.c.), and concentrated sulphuric acid (15 c.c.) was heated on the water-bath for an hour, cooled, diluted with water, and extracted with ether. The product was distilled (b. p. 235°/2—3 mm.), and the distillate recrystallised from acetic acid, from which the *spiran* (VIII; 8 g.) separated as colourless crystals, m. p. 82—83° (*Found : C, 91·8; H, 8·0. $C_{25}H_{26}$ requires C, 92·0; H, 8·0%). This hydrocarbon, which was saturated towards pyridine sulphate dibromide (compare Part I), was recovered entirely unchanged after heating with selenium at 310—320° for 24 hours. The resinous material from the original acetic acid mother-liquors was

similarly treated with selenium, but gave only a further quantity of the same spiran. This spiran, unlike its isomeride (X), gave no crystalline picrate in alcoholic solution.

(b) Dehydration of the carbinol with phosphoric oxide (1·5 parts) at 160° gave the same saturated hydrocarbon (VIII), m. p. 82—83°.

(c) The spiran (VIII) was also isolated when the indene (VII), diluted with carbon disulphide, was treated at 0° for 4 hours with anhydrous aluminium chloride.

β-5-*Tetralylethyl Alcohol*.—α-Naphthylamine was reduced to 5-aminotetralin under the conditions recommended by Morgan, Micklethwait, and Winfield (J., 1904, **85**, 744), and this was converted into 5-bromotetralin through the Sandmeyer reaction (Smith, *ibid.*, p. 729). An ice-cold Grignard solution prepared from 5-bromotetralin (49 g.), magnesium turnings (5·6 g.), and anhydrous ether (150 c.c.) was treated with ethylene oxide (14 g.). After keeping over-night at room temperature, the ether was distilled off and the residue was heated on the water-bath for an hour. The product was decomposed with ice and hydrochloric acid, extracted with ether, and the extract washed and distilled. The resulting alcohol (23 g.) formed a pale yellow liquid, b. p. 160°/12 mm. For analysis, it was purified through its 3 : 5-*dinitrobenzoate*, obtained by brief heating at 100° with 3 : 5-dinitrobenzoyl chloride in pyridine. After several crystallisations from benzene–*cyclo*hexane and then alcohol, this ester formed yellowish prismatic needles, m. p. 128—129° (†Found : C, 61·8; H, 4·8. $C_{19}H_{18}O_6N_2$ requires C, 61·6; H, 4·9%). Pure β-5-*tetralylethyl alcohol*, obtained by hydrolysis of this ester with alcoholic potassium hydroxide, formed a colourless viscous liquid, b. p. 120°/0·2 mm. (Found : C, 81·5; H, 9·1. $C_{12}H_{16}O$ requires C, 81·7; H, 9·2%).

β-5-*Tetralylethyl Chloride*.—This was obtained from the alcohol by means of thionyl chloride and dimethylaniline, and formed a pale yellow liquid, b. p. 155°/11—12 mm. (Found : C, 73·8; H, 7·6. $C_{12}H_{15}Cl$ requires C, 74·0; H, 7·8%).

1-*Hydroxy*-1-(β-5′-*tetralylethyl*)-7-*methyl*-4-iso*propylhydrindene*.—The condensation between the Grignard compound of tetralylethyl chloride (12 g.) and 7-methyl-4-*iso*propyl-1-hydrindone (V; R = H) (9·2 g.) was carried out just as the analogous reaction with naphthylethyl chloride. The *carbinol* (2·5 g.) was isolated from the crude reaction product by means of light petroleum, and was recrystallised from methyl alcohol, forming compact colourless crystals, m. p. 114·5—115° (Found : C, 86·1; H, 9·5. $C_{25}H_{32}O$ requires C, 86·1; H, 9·3%).

7-*Methyl*-4-iso*propylhydrindene*-1 : 1′-spiro-(4′ : 5′-*benz*)*hydrindene* (X).—The preceding carbinol (1 g.) was heated on the water-bath for an hour with concentrated sulphuric acid (1 c.c.) in glacial acetic acid (10 c.c.). The saturated resinous product was heated with selenium (1 g.) at 320° for 20 hours, and the product distilled at 0·05 mm. from a bath at 180—200°. The distillate was dissolved in a little ether, and the solution cooled in a freezing mixture. A small amount of crystalline material separated which, after recrystallisation from acetic acid, had m. p. 198—200°. This was probably methyl*iso*propylnaphthafluorene (III), but there was insufficient for identification. The ether was removed from the liquors, and the residue treated with picric acid (0·5 g.) in acetic acid. The resulting scarlet *picrate* of the spiran (X) was recrystallised from acetic acid; it then had m. p. 121·5—122° (*Found : C, 67·1; H, 5·2. $C_{25}H_{26},C_6H_3O_7N_3$ requires C, 67·0; H, 5·3%). This product was formed in good yield. The hydrocarbon regenerated from the pure picrate could not be obtained crystalline.

*Chrysofluorene from 2-Methyl-1-hydrindone.*

3-β-*Phenylethyl*-2-*methylindene* (XI).—The benzylmethylacetic acid required for this synthesis was prepared from benzyl chloride and ethyl sodiomethylmalonate (Conrad and Bischoff, *Annalen*, 1880, **204**, 177). 2-Methyl-1-hydrindone was obtained in 82% yield by the action of aluminium chloride on benzylmethylacetyl chloride, the conditions being those used by Ingold and Piggott (J., 1923, **123**, 1502) in an analogous case. The condensation between 2-methyl-1-hydrindone (12 g.) and the Grignard compound of β-phenylethyl chloride (14 g.) was effected in the usual way. The crude carbinol did not crystallise and was distilled in a vacuum, whereby it was dehydrated to the indene, b. p. 170°/1 mm. (yield, 15 g. = 80%). 3-β-*Phenylethyl*-2-*methylindene* (XI) was purified through its picrate, which was very easily dissociated, and was then distilled over sodium at 0·8 mm., forming a colourless liquid (Found : C, 92·0; H, 7·6. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%).

10-*Methyl*-3 : 4 : 10 : 11-*tetrahydro*-1 : 2-*benzfluorene* (XII).—An ice-cold solution of the indene (XI; 11·6 g.) in carbon disulphide (120 c.c.) was treated with anhydrous aluminium chloride (13·5 g.). After being kept at 0° for 3 hours the carbon disulphide solution was decanted from the aluminium chloride sludge, washed with dilute hydrochloric acid and with water, and distilled. The tetracyclic *hydrocarbon* (XII) was redistilled over sodium, forming a

colourless viscous liquid, b. p. 159°/0·8 mm. (yield, 9·5 g. = 82%). This was completely saturated and did not increase the colour of a picric acid solution (Found : C, 91·9; H, 7·7. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%).

*Chrysofluorene.*—The foregoing tetracyclic hydrocarbon (2·8 g.) was heated with selenium (2 g.) at 310—320° for 24 hours. The crystalline product was extracted with acetic acid, and the solution allowed to crystallise. It formed colourless plates (1·5 g. = 65% of the theoretical), m. p. 180—182° after slight sintering. Sublimation in a vacuum, followed by crystallisation from acetic acid, removed a trace of selenium and gave pure chrysofluorene, m. p. 182—183° alone or mixed with an authentic sample.

### 2′ : 1′-*Naphtha*-1 : 2-*fluorene and Derivatives.*

3-(β-5′-*Tetralylethyl*)-2-*methylindene* (XIII; R = R′ = H).—2-Methyl-1-hydrindone (11 g.) was added to an ice-cold Grignard solution prepared from β-5-tetralylethyl chloride (17·6 g.), magnesium turnings (2·2 g.), and anhydrous ether (100 c.c.). The crude carbinol was dehydrated by heating to 150° and the resulting indene was distilled in a vacuum (yield, 14·3 g. = 66%). The *picrate* crystallised from alcohol in scarlet plates, m. p. 115° (Found : C, 65·5; H, 5·4. $C_{22}H_{24}$,$C_6H_3O_7N_3$ requires C, 65·0; H, 5·25%). 3-(β-5′-*Tetralylethyl*)-2-*methylindene*, regenerated from the pure picrate and distilled over sodium, had b. p. 190°/0·3 mm., and crystallised from alcohol in colourless rhombs, m. p. 73° (Found : C, 91·3; H, 8·3. $C_{22}H_{24}$ requires C, 91·6; H, 8·4%).

10-*Methyl*-3 : 4 : 10 : 11 : 5′ : 6′ : 7′ : 8′-*octahydro*-2′ : 1′-*naphtha*-1 : 2-*fluorene* (XIV; R = R′ = H).—An ice-cold solution of the indene (XIII; R = R′ = H) (1 part) in carbon disulphide (10 parts) was treated at 0° for 3 hours with anhydrous aluminium chloride (1 part). Vacuum distillation of the product gave an 80% yield of a glass-like mass, b. p. 195°/0·4 mm., which became crystalline in light petroleum. After recrystallisation from alcohol, the pentacyclic *hydrocarbon* (XIV; R = R′ = H) formed colourless rhombs, m. p. 123·5—124° (Found : C, 91·2; H, 8·5. $C_{22}H_{24}$ requires C, 91·6; H, 8·4%). The same hydrocarbon was obtained by cyclisation of the indene with sulphuric acid in acetic acid at 100°.

2′ : 1′-*Naphtha*-1 : 2-*fluorene*.—(a) The foregoing methyloctahydro-compound (2·5 g.) was heated with selenium (3 g.) at 310—320° for 20 hours. After crystallisation from xylene, the product (1·35 g.) had m. p. 317°, after sintering, and was contaminated with selenium, which could not be removed by recrystallisation but was readily separated by fractional vacuum sublimation. The first fraction (250°/0·3 mm.) was mainly selenium; the naphthafluorene sublimed at 300°/0·3 mm. After recrystallisation from pyridine and then xylene, 2′ : 1′-*naphtha*-1 : 2-*fluorene* formed colourless glistening leaflets, m. p. 327—328°, in a bath pre-heated to 300° (†Found : C, 94·6; H, 5·5. $C_{21}H_{14}$ requires C, 94·7; H, 5·3%).

The brick-red 2 : 7-*dinitroanthraquinone complex*, prepared in xylene, had m. p. 249—251° (†Found : C, 74·7; H, 3·6; N, 5·1. $C_{35}H_{20}O_6N_2$ requires C, 74·4; H, 3·6; N, 5·0%).

(b) The dehydrogenation of (XIV; R = R′ = H) was effected by heating with selenium at 400—420° for 10 hours, and the product purified as described under (a). The two products were indistinguishable in their m. p.'s and mixed m. p.'s, and the identification of this sample of naphthafluorene was completed by oxidation to naphthafluorenone.

*Oxidation of* 2′ : 1′-*Naphtha*-1 : 2-*fluorene*.—The monoketone (XIV) could be obtained by oxidation with the calculated amount of sodium dichromate in acetic acid, but purification was troublesome, and it was better to use an excess of dichromate. This gave some triketone (XVII), which was readily separated from the monoketone (XVI) by fractional vacuum sublimation. A suspension of powdered 2′ : 1′-naphtha-1 : 2-fluorene (0·1 g.) in purified acetic acid (5 c.c.) was boiled for an hour with sodium dichromate (0·3 g.). The crystals which separated on cooling were sublimed at 0·2 mm. The orange sublimate formed at 220—240° was recrystallised from acetic acid, and formed reddish-orange needles, m. p. 207—208° (†Found : C, 90·1; H, 4·5. $C_{21}H_{12}O$ requires C, 90·0; H, 4·3%). 2′ : 1′-*Naphtha*-1 : 2-*fluorenone* (XVI) gave an intense purple solution in concentrated sulphuric acid, the colour afterwards changing to magenta. At 300—320° the dark red *triketone* (XVII) sublimed. It crystallised from acetic acid (in which it was extremely sparingly soluble) in microscopic dark red needles, m. p. 340—350° (decomp.), after darkening from 280° (†Found : C, 80·8; H, 3·3. $C_{21}H_{10}O_3$ requires C, 81·3; H, 3·25%). This keto-quinone, which gave a yellow solution in concentrated sulphuric acid, was also formed by further oxidation of the monoketone (XVI).

2 : 7-*Dimethyl*-4-iso*propyl*-1-*hydrindone* (V; R = Me).—Condensation of 3-chloromethyl-*p*-cymene (35 g.) with ethyl sodiomethylmalonate (4·5 g. sodium, 70 g. ethyl methylmalonate, and 80 c.c. benzene) gave an ester (53 g.), b. p. 175°/2 mm., which was hydrolysed, and the

malonic acid decarboxylated by heating to 200°. β-(3-p-*Cymyl*)-α-*methylpropionic acid* (31 g.) formed a colourless liquid, b. p. 160—162°/0·8 mm. (Found : C, 76·4; H, 9·1. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·15%). Dehydration of this acid to 2 : 7-*dimethyl*-4-iso*propyl*-1-*hydrindone* (V; R = Me) was effected by heating at 120° for an hour with an equal weight of stannic chloride. By repeating the dehydration twice with the acid which was recovered, 25 g. of acid were converted into 15·8 g. of the hydrindone, b. p. 160°/16 mm., which crystallised from light petroleum in colourless needles, m. p. 46—46·5° (Found : C, 83·3; H, 8·9. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%).

3-(β-5′-*Tetralylethyl*)-2 : 4-*dimethyl*-7-iso*propylindene* (XIII; R = Me; R′ = Pr$^{\beta}$).—Condensation between β-5-tetralylethylmagnesium chloride (from 19 g. tetralylethyl chloride) and 2 : 7-dimethyl-4-*iso*propyl-1-hydrindone (15 g.) was effected in the usual manner and gave 24 g. of the distilled indene, which was purified by conversion into its picrate in alcoholic solution. This *dipicrate* formed ruby-red needles, m. p. 119—119·5° (†Found : C, 57·0; H, 4·8. $C_{26}H_{32},2C_6H_3O_7N_3$ requires C, 56·8; H, 4·8%). The pure *hydrocarbon* (XIII; R = Me; R′ = Pr$^{\beta}$), regenerated from the picrate and distilled over sodium, formed a pale yellow gum, b. p. 218°/0·3 mm. (Found : C, 90·5; H, 9·4. $C_{26}H_{32}$ requires C, 90·6; H, 9·4%).

5 : 10-*Dimethyl*-8-iso*propyl*-3 : 4 : 10 : 11 : 5′ : 6′ : 7′ : 8′-*octahydro*-2′ : 1′-*naphtha*-1 : 2-*fluorene* (XIV; R = Me; R′ = Pr$^{\beta}$).—Cyclisation of the indene with aluminium chloride at 0° was complete in 3 hours. After distillation over sodium the pentacyclic *hydrocarbon* (XIV; R = Me; R′ = Pr$^{\beta}$), b. p. 215—220°/0·3 mm., formed a colourless brittle glass (75% yield) which could not be induced to crystallise. It was saturated and gave no picrate (Found : C, 90·55; H, 9·3. $C_{26}H_{32}$ requires C, 90·6; H, 9·4%).

5-*Methyl*-8-iso*propyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene* (III).—This was obtained in 80% yield when the octahydro-compound (XIV; R = Me; R′ = Pr$^{\beta}$) (3·5 g.) was heated with selenium (4 g.) at 310—325° for 24 hours. The product was extracted with benzene, and the filtered solution concentrated and treated with alcohol. The crystals (2·65 g.; m. p. 195—196°) were freed from a trace of selenium by fractional sublimation in a vacuum. The hydrocarbon sublimed at 230—240°/0·2 mm. The sublimate was recrystallised from benzene and then ethyl acetate, from which 5-*methyl*-8-iso*propyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene* (III) separated as slightly yellowish plates, m. p. 198° (*Found : C, 93·0, 93·1; H, 6·9, 6·9; *M*, Rast method, 291, 304. $C_{25}H_{22}$ requires C, 93·1; H, 6·9%; *M*, 322). The presence of 25 carbon atoms in the molecule was confirmed by an accurate determination of the molecular weight, for which we are indebted to Dr. Bernal and Miss Crowfoot.

A mixture of this methyl*iso*propylnaphthafluorene and the Diels hydrocarbon " $C_{25}H_{24}$ " melted at 170—188°. The faint yellow colour of the hydrocarbon (III), which was due to exposure of the solutions to light during recrystallisation, could be removed by boiling an acetic acid solution with zinc, or by shaking a benzene solution with concentrated sulphuric acid. The 2 : 7-*dinitroanthraquinone complex* of (III) crystallised from xylene in red needles, m. p. 261—262° (†Found : C, 75·4; H, 4·6. $C_{39}H_{28}O_6N_2$ requires C, 75·5; H, 4·55%).

5-Methyl-8-*iso*propyl-2′ : 1′-naphtha-1 : 2-fluorene was also obtained in good yield when the cyclisation of (XIII; R = Me; R′ = Pr$^{\beta}$) was effected with sulphuric acid in acetic acid at 100°, the cyclisation product being subsequently dehydrogenated with selenium.

5-*Methyl*-8-iso*propyl*-2′ : 1′-*naphtha*-1 : 2-*fluorenone*.—This was obtained by boiling a solution of the hydrocarbon (III; 0·3 g.) in purified acetic acid (20 c.c.) with sodium dichromate (0·9 g.) for 15 minutes. The clear solution was diluted with water, and the precipitate collected and recrystallised from acetic acid. The orange plates could be seen to be contaminated with some red needles. The monoketone was obtained pure by vacuum sublimation, followed by crystallisation from benzene–alcohol, and then ethyl acetate. 5-*Methyl*-8-iso*propyl*-2′ : 1′-*naphtha*-1 : 2-*fluorenone* formed golden plates, m. p. 197—198°, which gave the same colours with concentrated sulphuric acid as did the parent ketone (XVI) and the ketone formed by oxidation of the Diels hydrocarbon (*Found : C, 89·0; H, 5·95. $C_{25}H_{20}O$ requires C, 89·25; H, 6·0%).

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