264. *Studies in Tar Hydrocarbons. Part I. Reduction Products of Pyrene.*

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SINCE the discovery that pyrene is comparatively plentiful in, and can be readily isolated in quantity from, certain hydrogenated tar fractions (B.P. 435,254 of 1935) it has attracted renewed interest. In particular, the arrangement of the double bonds and the location of residual affinity or points of attack in this aromatic type are of theoretical interest (Goldschmiedt, *Annalen*, 1907, **351**, 231; Clar, *Ber.*, 1936, **69**, 1671).

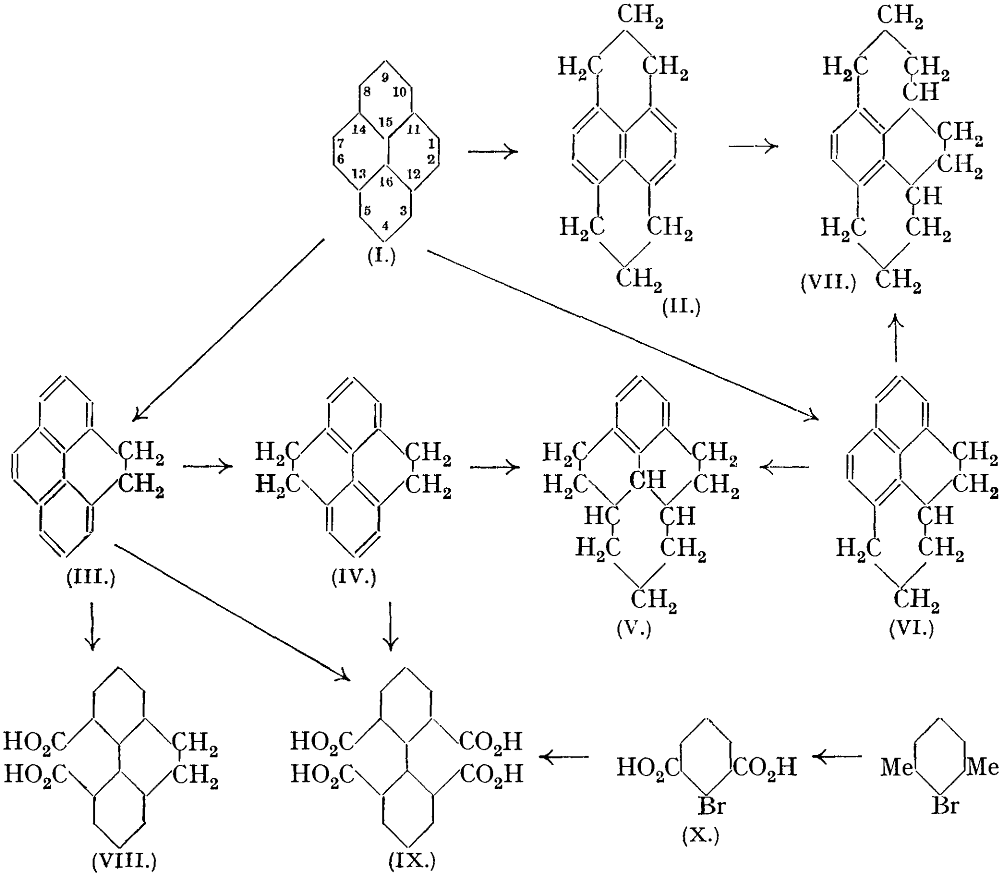
Catalytic Reduction of Pyrene.—Very few pyrene derivatives of ascertained constitution are known. With the object of preparing such derivatives as reference compounds from hydrogenated pyrenes, in which the possibilities of isomerism are less complicated, and which can be transformed by dehydrogenation into the corresponding pyrene derivatives, the preparation of the two known hexahydropyrenes was studied. One of these (Graebe, *Annalen*, 1871, **158**, 297) was proved to be the symmetrical or 3 : 4 : 5 : 8 : 9 : 10-isomeride (II) by Cook and Hewett (J., 1933, 401), who tried to reduce pyrene catalytically in tetralin solution with a nickel catalyst in order to obtain a good yield of this hexahydride, but favoured the sodium–boiling amyl alcohol method of Goldschmiedt, although it gave only 23% of a theoretical yield of the *s*.-hexahydride and less than 2% of a second hexahydropyrene—the *as*.-derivative (VI)—the only other pure product isolated.

In B.P. 435,254 it is stated that the presence of pyrene in hydrogenated tar oils is due to a characteristic resistance to hydrogenation but also that pyrene is hydrogenated at 300° with a nickel catalyst under an initial pressure of 80 atmospheres of hydrogen to the *s*.-hexahydride and that this may be converted into decahydropyrene at 210° with an initial pressure of 90 atmospheres. As these experimental conditions are by no means extreme, it became of interest to examine the effect of a molybdenum–sulphur–active charcoal catalyst on the reduction of pure pyrene. Contrary to expectation it was found that, even when the hydrocarbon was sealed with 100 atmospheres of hydrogen and 10% by weight of catalyst and heated to 400°, reduction occurred very slowly and at least two-fifths of the pyrene remained unchanged after 4 hours. *s*.-Hexahydropyrene (2% of theoretical) and a new 1 : 2-*dihydropyrene* (III), m. p. 132° (8% of theoretical), were the only other identifiable solid products. When the time of reaction was increased to 6 hours, other conditions remaining unchanged, there was still 43% of unreduced pyrene but, beside 7·5% of *s*.-hexahydride, the product contained 28% of a mixture of the 1 : 2-di- and the *as*.-hexa-hydropyrene difficult to separate, *ca*. 10% of a new 1 : 2 : 6 : 7-*tetrahydropyrene* (IV), m. p. 138°, 2% of naphthalene due to some cracking, and a residue of oily products obviously decahydropyrenes. These results were sufficient to show that good yields of either *s*.- or *as*.-hexahydropyrene are not obtainable by reduction with a molybdenum–sulphur–carbon catalyst at high temperatures.

Pestemer and Manchen (*Monatsh.*, 1936, **68**, 92) have, on the basis of ultra-violet absorption spectra, characterised a " dihydropyrene, m. p. 106° " and a " tetrahydropyrene, m. p. 84° " isolated by Zinke and Ristic (*Diss.*, Graz, 1936) from the products of sodium–amyl alcohol reduction of pyrene as mixtures of pyrene and *s*.-hexahydropyrene. They overlooked the likelihood that *as*.-hexahydropyrene was present in these mixtures.

Reductions with Sodium in Amyl Alcohol.—When pyrene was reduced as described by Cook and Hewett (*loc. cit.*), there was isolated from the product by an improved method 27% of the calculated amount of *s*.-hexahydride and a somewhat smaller yield of the *as*.-isomeride. Crystallisation of the more soluble, non-picrate-forming residue furnished a substance, m. p. 63°, which contained more hydrogen than a pure hexahydro-derivative and was apparently composed of equal mols. of tetra- and deca-hydropyrenes in some kind of association. The residue of liquid products, which do not form picrates in alcohol, consists evidently of decahydropyrenes. It is possible that careful regulation of the amount of sodium would permit the isolation of pure di- and tetrahydro-pyrenes, but under the conditions employed these as well as the *as*.-hexahydride, but unlike the *s*.-hexahydride, are very easily reduced. Thus 1 : 2-dihydropyrene gives the 1 : 2 : 6 : 7-tetrahydropyrene, which itself is easily reduced to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 12 : 13 : 16-*decahydropyrene* (V), m. p. 68°, isomeric with the 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-decahydropyrene (VII) prepared synthetically by v. Braun and Rath (*Ber.*, 1928, **61**, 956). The latter isomeride is in fact formed very slowly when *s*.-hexahydropyrene is treated with a great excess of sodium in boiling amyl alcohol. Reduction of *as*.-hexahydropyrene gives a product which apparently contains both decahydropyrenes and is only partly solid at room temperature. The diagram on p. 1300 summarises the course of the reduction reactions.

In the examination and separation of the di-, tetra-, hexa-, and deca-hydropyrenes great assistance is furnished by the variations in the stability of the corresponding picrates. Pyrene picrate is stable and sparingly soluble in alcohol and melts at 228°; mixtures containing pyrene and any hydrogenation product can be readily freed from pyrene by crystallisation from alcohol containing excess of picric acid. The picrates of *s*.-hexahydropyrene (II) and 1 : 2 : 6 : 7-tetrahydropyrene (IV) are not stable in presence of alcohol or ether, but can be formed in dry benzene. 1 : 2-Dihydropyrene (III) and *as*.-hexahydropyrene (VI) form picrates, m. p. 147° and 148°, which are quite stable in alcohol and have roughly the same solubility. When mixed, they slightly depress one another in m. p. The two decahydrides do not form picrates and are very soluble in both alcohol and petrol.



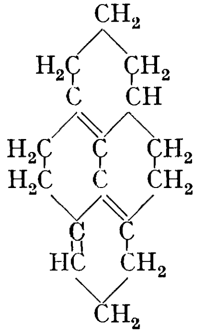
Constitutions of 1 : 2-*Dihydro*-, 1 : 2 : 6 : 7-*Tetrahydro*-, 1 : 2 : 3 : 4 : 5 : 6 : 7 : 12 : 13 : 16- *and* 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-*Decahydro-pyrenes.*—The evidence for the assigned constitutions of the di- and the tetra-hydride (III and IV) is based on oxidation. Both, when oxidised with potassium permanganate, furnished diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid. An authentic specimen of this acid was prepared by an improved method from *m*-2-xylidine through 2-*bromo*iso*phthalic acid* (X). No alternative formulation of the tetrahydro-derivative is, therefore, possible and the dihydro-derivative must be either 1 : 2- or 1 : 6-dihydropyrene. When oxidised with hydrogen peroxide in acetic acid, it gave a substance whose composition and properties agreed with 9 : 10-*dihydrophenanthrene*-4 : 5-*dicarboxylic acid* (VIII). This rules out the 1 : 6-orientation, since the two hydrogen atoms must be homonuclear.

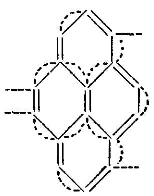
Of the ten hydrogen atoms in the decahydride prepared from the tetrahydride, the positions of four have been determined. The tetrahydride is a diphenyl derivative, as its oxidation clearly shows, and would be expected to be reduced fully in one aromatic ring. When treated with boiling potassium permanganate solution, the decahydride is not readily destroyed and no hemimellitic acid could be isolated from the small amount of acidic oxidation product, but this decahydride is not identical with the decahydride prepared from the *s*.-hexahydropyrene and the assigned formula, 1 : 2 : 3 : 4 : 5 : 6 : 7 : 12 : 13 : 16-decahydropyrene (V), is preferred to others, such as (XI), which would require the existence of non-aromatic double bonds.

Similar grounds justify the formula assigned to the decahydride derived by reduction of *s*.-hexahydropyrene, of which the constitution as 3 : 4 : 5 : 8 : 9 : 10-hexahydride (II) and therefore as a naphthalenoid hydrocarbon was determined by Cook and Hewett (*loc. cit.*). The melting point of this 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-decahydropyrene (VII) was higher than is given by v. Braun and Rath for the synthetical specimen. It may be observed that possibilities of *cis-trans* isomerism of the decalin type exist in both decahydrides, although so far unrealised. It is possible that v. Braun and Rath's synthetical specimen contained a different ratio of the two isomerides which accounts for its lower m. p. A liquid decahydride is referred to by Matsuno and Han (*Bull. Chem. Soc. Japan*, **1936**, **11**, 321), who do not state its origin but assign to it the formula given by v. Braun and Rath to the crystalline synthetical specimen. If this liquid were obtained, as seems likely, by the catalytic hydrogenation of pyrene, it may contain five isomerides, because the 1 : 2 : 3 : 4 : 5 : 6 : 7 : 12 : 13 : 16-decahydride derived from the 1 : 2 : 6 : 7-tetrahydride will be present in addition (3 forms).

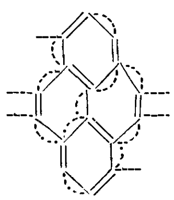
The Structure of Pyrene.—The arrangement of the double bonds in the four nuclei excited the attention of Goldschmiedt (*loc. cit.*), who put forward the Thiele formula (XII), which contains a *p*-quinonoid nucleus, on the basis of the persistent yellow colour of the hydrocarbon.

(XI.)

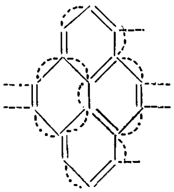




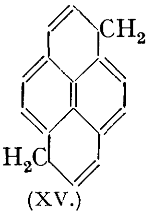
(XII.)



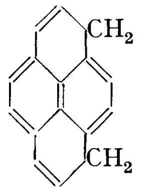
(XIII.)



(XIV.)



(XV.)



(XVI.)

Winterstein, Schön, and Vetter (*Z. physikal. Chem.*, **1934**, **230**, 146) showed that the colour of the hydrocarbon prepared from tar oils was due to a so-called " chrysogen," pure pyrene being colourless. It is curious that, although the formulation predicted reactivity in the 1 : 2-positions, no evidence of such reactivity was adduced or even sought. When pyrene reacts with aryl chlorides, condensation occurs in the 3 : 8- and 3 : 10-positions (Scholl and Seer, *Annalen*, **1912**, **394**, 121). There is no evidence to differentiate between a 3 : 8- and 3 : 10-orientation for the quinone formed by oxidation. In the latest study of the structure of pyrene based on absorption spectra, Clar (*Ber.*, **1936**, **69**, 1671) finds evidence that the 3 : 8-positions are reactive, but the 1 : 2-positions are subsidiary centres. Goldschmiedt's formula must therefore be rejected.

There are only two other acceptable arrangements of the double bonds (as in XIII and XIV) and application of Thiele's principles leads to the conclusion that (XIV) would be the equivalent of Goldschmiedt's formula (XII) predicting 3 : 10-activity and therefore inadmissible, although its acceptance would be more fully in accordance with the principle set up by Fries, Walter, and Schilling (*Annalen*, **1935**, **516**, 248) that in a polynuclear hydrocarbon the double bonds are arranged to give the maximum number of benzenoid rings.

There is no difficulty in explaining the experimental facts of hydrogenation on either formula. If the 3 : 8- or 3 : 10-carbon atoms are attacked initially, the first formed dihydrides (XV and XVI) will in either case be rapidly reduced to the stabler *s.*-hexahydropyrene (II) in which the two unattacked nuclei have become naphthalenoid. Again, if the initial attack occurs in the 3 : 2-, 3 : 1-, 3 : 6- or 3 : 7-positions in either (XIII) or (XIV), it will continue until finally the *as.*-hexahydropyrene (VI, again a naphthalenoid system) is formed. The stable 1 : 2-dihydropyrene (III) results if initial attack occurs in the 1 : 2- or 6 : 7-positions. This is regarded as phenanthrenoid, because when subjected to further reduction it is attacked (at the 6 : 7-positions) in what corresponds to the 9 : 10-positions of phenanthrene (cf. Burger and Mosettig, *J. Amer. Chem. Soc.*, 1935, **57**, 2731) and the resultant tetrahydropyrene (IV) has the stable benzenoid arrangement of bonds present in diphenyl. If initial attack occurs at the 1 : 6- or 1 : 7-positions, a stable arrangement is not reached until four hydrogen atoms have been added to give the benzenoid tetrahydropyrene (IV).

It will be seen that the course of hydrogenation gives experimental proof, hitherto lacking, that reactive centres are present in the 1 : 2- and possibly the 6 : 7-positions in the pyrene nucleus as well as in the 3 : 8- or 3 : 10-positions. If the structure of pyrenequinone is definitely decided as a 3 : 8-derivative, (XIII) must be accepted as the best representation of the structure and reactivity of pyrene.

EXPERIMENTAL.

Catalytic Hydrogenation of Pyrene with a Molybdenum–Sulphur–Carbon Catalyst.—(a) *Short reaction period :* 1 : 2-*Dihydropyrene* (III). Pyrene (50 g.) was placed in a 500 c.c. autoclave with hydrogen at 100 atms. and a catalyst made by impregnating 5 g. of active charcoal with a solution of 1 g. of molybdenum trioxide in aqueous ammonia, drying the mixture at 100°, and adding 1 g. of flowers of sulphur. The temperature was raised to 400° and maintained for 4 hours. After cooling, the pressure was 80 atms. The product, a solid, was dissolved away from the catalyst with ether and treated in boiling alcohol (500 c.c.) with 50 g. of picric acid. After removal of 40 g. of pyrene picrate, m. p. 220°, by crystallisation (it is only slightly soluble in cold alcohol) the mother-liquor was concentrated; a mixture of colourless needles of *s.*-hexahydropyrene and red needles of the mixed picrates of 1 : 2-dihydro- and *as.*-hexahydro-pyrene slowly crystallised. These were separated by repeated washing with cold alcohol, which dissolved the picrates more rapidly than the hydrocarbon. *s.*-Hexahydropyrene (1 g.) was obtained pure, m. p. 132°, not depressed by a specimen made by Goldschmiedt's method. The picrates were purified from traces of pyrene picrate by repeated extraction with cold alcohol and by crystallisation and a yield of 8 g., m. p. 142—149°, obtained, but this still contained some of the picrate of *as.*-hexahydride, as the hydrocarbon recovered after treatment with aqueous ammonia melted at 122°. On recrystallisation from alcohol, pure 1 : 2-*dihydropyrene* (II) (1·5 g.) was obtained in colourless satin-lustred flakes, m. p. 132° (Found : C, 93·7, 93·8; H, 6·0, 6·1. $C_{16}H_{12}$ requires C, 94·1; H, 5·9%). The *picrate* crystallised in bright red needles, m. p. 147° (Found : C, 60·7; H, 3·7. $C_{16}H_{12},C_6H_3O_7N_3$ requires C, 60·9; H, 3·5%), fairly soluble in alcohol but only very slightly soluble in petrol (b. p. 40—60°) ; it appeared to be rather more stable than the picrate of *as.*-hexahydropyrene, which it otherwise closely resembled. A mixture with the latter, m. p. 148°, melted at 143°.

When heated at 300° for 6 hours with selenium, the hydrocarbon was dehydrogenated to pyrene, isolated in good yield and identified by comparison with an authentic specimen.

(b) *Longer reaction period :* 1 : 2 : 6 : 7-*Tetrahydropyrene* (IV). Pyrene (100 g.) was hydrogenated in a 2 l. autoclave for 6 hours, all other conditions being as in (a). After removal of pyrene (43 g.) as picrate the product yielded 61·0 g. of mixed picrates of di- and *as.*-hexa-hydropyrene, m. p. *ca.* 140°, and 7·5 g. of pure *s.*-hexahydropyrene. The residual material (18 g., only partly solid) was warmed with 10 g. of picric acid till all had dissolved and the cooled mixture was triturated with petrol (b. p. 40—60°) to remove the hydrocarbons which did not form stable picrates. Picric acid and fairly pure 1 : 2-dihydropyrene picrate remained, but some 1 : 2-dihydropyrene passed into the petrol solution and it was only completely removed from the non-picrate-forming hydrocarbons by a second warming with picric acid and trituration with cold petrol. After removal of dihydropyrene the liquid portion of the hydrocarbons was separated, and the remaining solid (8 g.) fractionally crystallised from alcohol to yield roughly equal amounts of *s.*-hexahydropyrene and the more soluble 1 : 2 : 6 : 7-*tetrahydropyrene* (IV).

The liquid portion of the residual hydrocarbons was fractionally distilled in a vacuum; the most volatile portion crystallised and was recognised as naphthalene (2 g.); the higher-boiling fractions also crystallised slowly in part and from the solid a little more of both the *s*.-hexahydro- and the tetrahydro-pyrene was separated.

Considerable difficulty was experienced in characterising the hydrocarbon material recovered from the 61 g. of mixed picrates, m. p. *ca.* 140°. It boiled constantly at 228°/26 mm. and the m. p., originally 105—110°, slowly rose on crystallisation from alcohol to 111—113°; it then did not change further. The crystals were homogeneous, colourless flakes (Found: C, 93·6, 93·65; H, 6·8, 6·7. $C_{16}H_{12}$ requires C, 94·1; H, 5·9%. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%) with composition intermediate between di- and tetra-hydropyrene. When admixed with pure 1 : 2-dihydropyrene, m. p. 132°, the m. p. was slightly raised and with pure *as*.-hexahydropyrene, m. p. 105°, slightly lowered. Reduction showed that it consisted essentially of these two hydrocarbons in close association either as mixed crystals or as a compound (1 or 2 mols. of dihydro- to 1 mol. of *as*.-hexahydro-pyrene). The hydrocarbon (14 g.), m. p. 111—113°, was dissolved in 500 c.c. of boiling amyl alcohol, and 14 g. of sodium added in pieces. The product was worked up as described in the reduction of pure 1 : 2-dihydropyrene (below) and consisted of non-picrate-forming hydrocarbons; the least soluble and highest melting was pure 1 : 2 : 6 : 7-tetrahydropyrene (2 g.) identical with the specimen obtained by catalytic hydrogenation. An intermediate fraction formed homogeneous colourless needles of constant m. p. 73°, but appeared to be deca- and tetra-hydropyrenes in close association (Found: C, 90·8; H, 8·7%). The liquid portion contained the two isomeric decahydropyrenes (see reduction of *as*.-hexahydropyrene, below) in a subfraction of b. p. 148—150°/2 mm. (Found: C, 90·9; H, 9·0%).

1 : 2 : 6 : 7-Tetrahydropyrene (IV) is very soluble in petrol, benzene or ether and crystallises from alcohol, in which it is moderately readily soluble, in thin colourless flakes, m. p. 138° (Found: C, 93·1; H, 6·9. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). It is rather more soluble in alcohol than *s*.-hexahydropyrene, m. p. 132°, but has no tendency to associate or form mixed crystals with the latter. When mixed with *s*.-hexahydropyrene, its m. p. is depressed to 99—110°, but with 1 : 2-dihydropyrene, m. p. 132°, only a slight depression to 130° is noticed. The hydrocarbon is dehydrogenated to pyrene by heating with selenium for 6 hours at 300°.

Reduction of Pyrene with Sodium and Amyl Alcohol.—Following Cook and Hewett (J., 1933, 404), 66 g. of sodium were added gradually to 650 c.c. of boiling amyl alcohol containing 40 g. of pyrene. When most of the sodium had been added, the mixture was frequently shaken in order to granulate the metal and increase its activity. When all the sodium had dissolved (4 hours), steam was passed to remove the amyl alcohol. The reduction product was extracted by ether from the cooled aqueous suspension and dissolved in boiling alcohol, to which 40 g. of picric acid were added. On cooling, a mixture of *s*.-hexahydropyrene and the picrate of *as*.-hexahydropyrene crystallised. Pure *s*.-hexahydride (9·5 g.) (II) was obtained by washing the mixed crystals repeatedly with cold alcohol. The alcoholic liquors were evaporated, and successive crops of the picrate of *as*.-hexahydride removed, until only picric acid crystallised. All the crude picrate was triturated with cold petrol (b. p. 40—60°), which extracted the non-picrate-forming hydrocarbons. These were recovered and, crystallised from alcohol, yielded 1·5 g. of *s*.-hexahydride, and a smaller amount of a more stable, apparently homogeneous, substance crystallising in colourless flakes, m. p. 63° (Found: C, 91·7, 91·9; H, 8·2, 8·4%). This is evidently composed of equal amounts of tetrahydropyrene and one or both of the isomeric decahydropyrenes (see below) in association as mixed crystals or a loose compound ($C_{16}H_{14},C_{16}H_{20}$ requires C, 91·9; H, 8·1%).

The picrate (30 g., m. p. 143°) was decomposed by aqueous ammonia and gave 9 g. of pure *as*.-hexahydropyrene (VI) crystallising in flakes from alcohol, m. p. 106° (Found: C, 92·35; H, 7·6. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%).

Reduction of 1 : 2-*Dihydro-*, 1 : 2 : 6 : 7-*Tetrahydro-*, 3 : 4 : 5 : 8 : 9 : 10(s.)- *and* 1 : 2 : 3 : 4 : 5 : 12-(as.)-*Hexahydro-pyrenes.*—Reduction of all these derivatives with sodium and amyl alcohol and examination of the products were carried out on the same lines as described under pyrene, an essential step being treatment with picric acid and separation of any picrate-forming hydrocarbon.

(a) 1 : 2-*Dihydropyrene* (III). The hydrocarbon (0·5 g.) was treated with 0·75 g. of sodium. No isolable amount of picrate-forming substance was present. The non-picrate-forming product was recrystallised from alcohol and formed colourless flakes, m. p. 138°, identical with pure 1 : 2 : 6 : 7-tetrahydropyrene, isolated from the products of catalytic hydrogenation of pyrene. In the mother-liquors were substances melting below 100°, consisting of decahydropyrenes due to the use of excess of sodium in the reduction. There was no sign of the formation of *s*.-hexahydropyrene, which under these conditions would not have been further reduced to any great extent.

(b) 1 : 2 : 6 : 7-*Tetrahydropyrene*: *Preparation of* 1 : 2 : 3 : 4 : 5 : 6 : 7 : 12 : 13 : 16-*decahydropyrene* (V). The product obtained in good yield from 1 g. of hydrocarbon and 4 g. of sodium was at first an oil which did not form a picrate, but after distillation in a vacuum and crystallisation from alcohol, in which it was quite soluble, it formed colourless needles or elongated plates, m. p. 68°, of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 12 : 13 : 16-*decahydropyrene* (V) (Found: C, 90·8; H, 9·0. $C_{16}H_{20}$ requires C, 90·6; H, 9·4%). When heated, this hydrocarbon had a faint terpene-like odour.

(c) 3 : 4 : 5 : 8 : 9 : 10-*Hexahydropyrene* (s.): *Preparation of* 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-*decahydropyrene* (VII). The hydrocarbon (3 g.) was treated with 30 g. of sodium and the product, solid and non-picrate-forming, was fractionally crystallised from alcohol. It yielded *ca*. 1 g. of pure and unchanged *s*.-hexahydropyrene, m. p. 132°, and an equal amount of a lower-melting substance, which was more soluble in alcohol, from which it separated in colourless flakes, m. p. 68°. This hydrocarbon, 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-*decahydropyrene* (VII) (Found: C, 90·5; H, 9·1%), is isomeric with the foregoing decahydride and on admixture the m. p. falls to 46°. In the mother-liquors was present an oily hydrocarbon product still richer in hydrogen, possibly "perhydropyrene" (Matsuno and Han, *loc. cit.*).

(d) 1 : 2 : 3 : 4 : 5 : 12-*Hexahydropyrene* (as.). The hydrocarbon (5 g.) was reduced with 20 g. of sodium; no picrate-forming fraction was found in the product, which was a colourless viscid oil. After distillation in a vacuum the fraction, b. p. 148—150°/2 mm., crystallised on cooling to 0°, but melted almost completely at room temperature. The low m. p. shows that it contains both the 1 : 2 : 3 : 4 : 5 : 6 : 7 : 12 : 13 : 16- and the 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-decahydride (Found: C, 90·6; H, 9·2. Calc. for $C_{16}H_{20}$: C, 90·6; H, 9·4%). No attempt was made to separate them. The higher-boiling fractions contained a low-melting solid substance, forming homogeneous, colourless needles, m. p. 55°, when crystallised from alcohol and apparently composed of mixed crystals of deca- and hexa-hydropyrene (Found: C, 90·3; H, 8·9%).

Oxidation of 1 : 2-*Dihydro-*, 1 : 2 : 6 : 7-*Tetrahydro-*, 1 : 2 : 3 : 4 : 5 : 12-*Hexahydro-*, *and* 1 : 2 : 3 : 4 : 5 : 6 : 7 : 12 : 13 : 16-*Decahydro-pyrenes*.—(a) 1 : 2-*Dihydropyrene*. (i) *With hydrogen peroxide*. The hydrocarbon (1 g.) was dissolved in a little warm acetic acid and kept at about 100° during 6 hours, hydrogen peroxide solution ("100 vols.") being added in small portions until no further colour changes occurred. The solution was then cooled, neutralised with sodium carbonate, extracted with ether to remove neutral material, made acid, and evaporated to dryness to remove acetic acid. From the residue ether extracted an acid substance (0·1 g.) which crystallised from acetone in cream flakes, m. p. 265°. Analysis showed this to be 9 : 10-*dihydrophenanthrene*-4 : 5-*dicarboxylic acid* (VIII) (Found: C, 71·7; H, 4·7. $C_{16}H_{12}O_4$ requires C, 71·8; H, 4·4%). The dihydropyrene is resistant to chromic acid in boiling acetic acid and some at least was recovered unattacked after 4 hours.

(ii) *With potassium permanganate*. The hydrocarbon (1 g.) was suspended in 400 c.c. of boiling water to which 30 g. of potassium permanganate were slowly added until no crystals of the hydrocarbon floated in the cooled solution (2 days). The excess of permanganate was then destroyed with hydrogen peroxide, and the boiling solution filtered from precipitated manganese dioxide, which was extracted three times with boiling water. The combined solutions, containing the potassium salt of the acidic oxidation product, were evaporated to small bulk, made acid, and thoroughly extracted with ether. A small amount of diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid, forming iridescent flakes, m. p. 400°, identical in all respects with a specimen made synthetically from *m*-2-xylidine (below), was isolated by crystallisation of the crude acid oxidation product from acetone.

(b) 1 : 2 : 6 : 7-*Tetrahydropyrene*. Like the dihydropyrene, the tetrahydride (0·5 g.) was oxidised very slowly when heated with potassium permanganate (7·0 g.) in boiling aqueous suspension, but after 2 days no unchanged hydrocarbon remained and the acid oxidation product contained diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid, which was isolated as described above and compared with an authentic specimen.

(c) 1 : 2 : 3 : 4 : 5 : 12-*Hexahydropyrene* (as.). Cook and Hewett (*loc. cit.*) remark that this hydrocarbon is resistant to alkaline permanganate, but it was found to have disappeared after boiling for 3 days in aqueous suspension with excess of potassium permanganate. The resinous acidic oxidation product was very small in amount and no crystalline individual substance could be isolated therefrom.

(d) 1 : 2 : 3 : 4 : 5 : 6 : 7 : 12 : 13 : 16-*Decahydropyrene*. The hydrocarbon (5·0 g.) was suspended in boiling water and treated with 50 g. of potassium permanganate until none remained unoxidised. The acidic oxidation product, isolated as described, was small in amount and contained aliphatic acids in addition to resinous substances. No hemimellitic acid could be isolated.

Preparation of 2-*Bromo*iso*phthalic* (X) *and Diphenyl*-2 : 6 : 2′ : 6′-*tetracarboxylic Acids* (IX).—James, Kenner, and Stubbings (J., 1920, **117**, 774) obtained methyl diphenyl-2 : 6 : 2′ : 6′-tetracarboxylate by treating methyl 2-iodo*iso*phthalate with copper bronze, but the following process is more expeditious. A solution of *m*-2-xylidine (72 g.) in 72 c.c. of concentrated sulphuric acid and 360 c.c. of water was diazotised at 5—10° with an aqueous solution of 43 g. of sodium nitrite and poured into a cold solution of cuprous bromide (made by saturating 65 g. of potassium bromide and 130 g. of copper sulphate in 576 c.c. of water with sulphur dioxide) in 270 c.c. of hydrobromic acid (b. p. 125—127°). After decomposition at 100° the oily 2-bromo-*m*-xylene, purified by extraction with ether and by distillation from solid potassium hydroxide (yield, 27 g.; b. p. 200—201°), was suspended in 500 c.c. of boiling water and oxidised with 100 g. of potassium permanganate, added gradually. After the excess of permanganate had been destroyed, the solution was filtered from precipitated manganese dioxide, concentrated, cooled, acidified, and extracted with ether. The acid product (24·5 g., m. p. 212°) obtained after removal of the ether contained 2-bromo*iso*phthalic acid contaminated with 22% of 2-hydroxy*iso*phthalic acid. The mixed methyl esters, obtained by saturating a solution of the acid product in dry methanol with hydrogen chloride and distilling, boiled at 188°/20 mm. (yield, quantitative). Pure *methyl* 2-*bromo*iso*phthalate* was obtained, by shaking the mixture in ethereal solution with cold dilute caustic soda solution and water, as a colourless liquid, b. p. 190—191°/22 mm., which did not set on keeping (Found : Br, 29·1. $C_{10}H_9O_4Br$ requires Br, 29·3%). It was hydrolysed quantitatively by 2 hours' boiling with concentrated hydrochloric acid; 2-*bromo*iso*phthalic acid* (X), m. p. 218°, crystallised in colourless needles on cooling (Found : Br, 32·7. $C_8H_5O_4Br$ requires Br, 32·7%).

When methyl 2-bromo*iso*phthalate (5 g.) was heated with 2 g. of copper bronze, a vigorous reaction began at 180°. After being kept at 200° for ¼ hour, the product was cooled and extracted with ether. From this extract, 2 g. of methyl diphenyl-2 : 6 : 2′ : 6′-tetracarboxylate, m. p. 124—125°, were obtained. On hydrolysis this gave the acid, quantitatively, in colourless flakes, m. p. 400°. When the acid melts, it decomposes and a yellow sublimate, m. p. 225°, appears. A further property useful in characterisation is the sparing solubility in ether.

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