75. *Catalytic Hydrogenation of Pyrene.*

By J. M. L. Cameron, J. W. Cook, and Walter Graham.

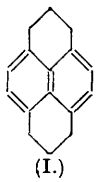
Conditions have been determined for the catalytic hydrogenation of pyrene to hexa-, deca-, and hexadecahydrides. *s*-Hexahydropyrene has been converted into the *ketone* (VII).

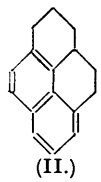
The increasing availability of the tetracyclic aromatic hydrocarbon, pyrene (see *Ann. Reports*, 1942, **39**, 157), and the development of its chemistry (Vollmann *et al.*, *Annalen*, 1937, **531**, 1) make this hydrocarbon a useful starting point for many synthetic projects. For such a purpose we have sought a convenient process for the preparation of *s*-hexahydropyrene (I), which was prepared by Cook and Hewett (J., 1933, 398) by Goldschmiedt's method (*Annalen*, 1907, **351**, 226) by reduction of pyrene with sodium and amyl alcohol. They obtained *s*-hexahydropyrene in 25% yield, and *as*-hexahydropyrene (II) in 7·5% yield by this process, these yields being increased to 27% and 22%, respectively, by Coulson (J., 1937, 1298), who also studied the hydrogenation of pyrene over a molybdenum–sulphur–active charcoal catalyst. Coulson found pyrene to be rather resistant to hydrogenation, and this accords with the experience of Kaghira (*Bull. Chem. Soc. Japan*, 1931, **6**, 251), who stated that hydrogenation of pyrene with a nickel catalyst was more difficult than that of other hydrocarbons, but claimed a theoretical yield of hexahydropyrene by hydrogenation at 300° for 52 hours.

We have found that pyrene is very readily hydrogenated under suitable conditions. With Raney nickel in *cyclo*hexane at 100° and 130 atm., it was completely hydrogenated to a liquid mixture of hexadecahydropyrenes (III) in 6 hours. When the temperature of hydrogenation was increased to 150—160°, the composition of the mixture was altered and the liquid product deposited crystals of the pure *hexadecahydropyrene* (III), m. p. 90°. Hydrogenation of pyrene with Raney nickel in ethanol at 150° and 160 atm. led to a mixture of decahydropyrenes, from which was obtained a stereochemically pure constituent, m. p. 128° (IV or V). When hydrogenation was carried out in ethanolic solution with copper chromite at 100—110° and 125 atm., it proceeded to the stage of hexahydride, both isomerides (I and II) being isolated. In a series of 7 experiments the yield of the *s*-hexahydride (I) varied between 35% and 45% (average, 40%) and the yield of *as*-hexahydride between 8% and 28% (average, 11%). This is the most satisfactory method yet found for the preparation of *s*-hexahydropyrene, and with more efficient methods of separation of the isomerides the yields would undoubtedly be considerably higher. Samples of pyrene which resisted hydrogenation on account of the presence of catalyst poison were readily susceptible to hydrogenation with a new batch of catalyst.

The ease with which pyrene is completely hydrogenated is of interest in view of the difficulty of hydrogenating the last double bond of phenanthrene (Durland and Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 1501) and chrysene

(v. Braun and Irmisch, *Ber.*, 1932, **65**, 883; Spilker, *Angew. Chem.*, 1935, **48**, 368). Although the perhydrides of condensed-ring aromatic hydrocarbons are sometimes resistant to dehydrogenation (Cook, McGinnis, and


(I.)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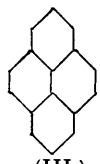
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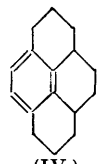
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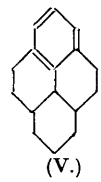

(V.)

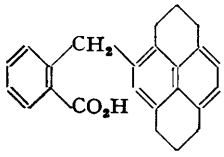
and Mitchell, J., 1944, 286), the perhydropyrene (III), m. p. 90°, was smoothly dehydrogenated to pyrene by palladium-black at 300° in 1½ hours.

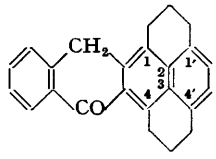
The *decahydropyrene*, m. p. 128°, is different from the three decahydropyrenes previously described (v. Braun and Rath, *Ber.*, 1928, **61**, 956; Coulson, *loc. cit.*). An attempt was made to distinguish between the two possible structures (IV and V) by oxidation of the hydrocarbon with dilute nitric acid, followed by esterification of the acid product. From the mixture of esters was isolated a small amount of a compound, m. p. 110°. The quantity was insufficient for exhaustive purification, but the analytical figures were in good agreement with those for *methyl 5-nitrohemimellitate*. The isomeric 4-nitro-ester has m. p. 144° (Cook and Hewett, J., 1934, 371). This structure has not been confirmed by independent synthesis, but if it is correct the decahydropyrene must be represented by formula (V).

Hydrogenation of anthracene with copper chromite at 100° gave 9 : 10-dihydroanthracene in 90% yield. This procedure is more convenient than the older method of reduction with sodium and amyl alcohol. When the hydrogenation was carried out at 150°, a considerable proportion of the anthracene was converted into *s*-octahydroanthracene.

Condensation of *s*-hexahydropyrene (I) with phthalic anhydride by means of anhydrous aluminium chloride proceeded normally to give a phthaloylic *acid*, which gave only amorphous brown substance that could not be purified when dehydration to a quinone was attempted by benzoyl chloride in boiling α-chloronaphthalene (compare Vollmann, *et al.*, *loc. cit.*) or by boiling benzoyl chloride containing a trace of sulphuric acid (Waldmann, *J. pr. Chem.*, 1938, **150**, 121). The phthaloylic acid was reduced by prolonged treatment with zinc dust and boiling alkali to 1-(o-*carboxybenzyl*)-s-*hexahydropyrene* (VI), which was dehydrated by acetic acid and acetic anhydride containing zinc chloride to 1 : 1′-4 : 4′-*bis*(*trimethylene*)-2 : 3-*benz*-10-*anthrone* (VII).

(VI.)





(VII.)

The formation of the anthrone rather than the anthranyl acetate under these conditions is noteworthy (compare Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1937, **59**, 1032) and illustrates the known reluctance of a dihydronaphthacene structure to pass into a naphthacene structure (Fieser, *ibid.*, 1931, **53**, 2329). The anthrone (VII) showed no tendency whatever to enolise, even with alcoholic potash, and gave no acetate with acetic anhydride in pyridine at 100°. It was recovered unchanged from an attempt to condense it with phenylmagnesium bromide (in boiling ether and in boiling benzene), and also after attempted reduction by the Clemmensen–Martin method (48 hours) and by Clar's zinc-dust fusion method (*Ber.*, 1939, **72**, 1645). In view of the inertness of this ketone its investigation was not pursued.

Experimental.

Hexahydropyrenes.—A suspension of pyrene (35 g.) and Adkins's copper chromite catalyst (8 g.) in ethanol (500 c.c.) was heated with hydrogen in a steel autoclave at 100—105° for 6 hours, with continuous agitation. The initial pressure was 130 atm. The autoclave was opened, and its contents heated to boiling and filtered from catalyst. On cooling, the solution deposited colourless needles of *s*-hexahydropyrene (I) (13 g.), m. p. 132—134°. Concentration of the mother-liquors gave two further crops of crystals, m. p. 90—93° (11 g.) and 93—97° (8 g.). These two fractions were treated separately with picric acid in ethanol, and by fractional crystallisation there were obtained a further quantity (3·1 g.) of *s*-hexahydropyrene and the picrate of *as*-hexahydropyrene (compare Cook and Hewett, *loc. cit.*). This picrate, on treatment with sodium carbonate, gave pure *as*-hexahydropyrene (II) (3·8 g.), m. p. 105°. In other experiments the yields of the two isomerides varied somewhat (see above).

Decahydropyrenes.—A suspension of pyrene (15 g.) and Raney nickel (8 g.) in ethanol (250 c.c.) was heated and stirred with hydrogen under pressure at 150° for 6½ hours. The initial pressure was 160 atm. The filtered solution was distilled under reduced pressure, and gave a colourless liquid (15 g.), b. p. 185—187°/14 mm. After a week in the refrigerator the small amount of crystals which had separated was collected and recrystallised twice from ethanol. This solid *decahydropyrene* (V) formed long, colourless needles, m. p. 127—129° (Found : C, 90·3; H, 9·3. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%). The liquid mixture of decahydropyrenes from which these crystals had separated was redistilled, and had b. p. 183—185°/13 mm. (Found : C, 90·3; H, 9·7%). For oxidation, the crystalline hydrocarbon (0·25 g.) was heated in a sealed tube at 175—180° for 6 hours with concentrated nitric acid (2·5 c.c.) and water (5 c.c.). After cooling, the solution was diluted with water and filtered, and the filtrate evaporated to dryness. The crystalline residue was dissolved in dilute aqueous ammonia, the excess of which was removed by boiling, and the solution was treated with aqueous silver nitrate. The precipitated silver salts (0·35 g.) were dried and their suspension in benzene (4 c.c.) and methyl iodide

(1 c.c.) was boiled for 12 hours. Evaporation of the filtered solution gave a viscous liquid which became crystalline in methanol. Repeated crystallisation from methanol (charcoal) gave tufts of colourless needles, m. p. 110—111°, consisting of *methyl 5-nitrohemimellitate* (Found: C, 48·2; H, 3·5; N, 4·7. $C_{12}H_{11}O_8N$ requires C, 48·5; H, 3·7; N, 4·6%). A fraction from the liquors had m. p. 99—100°, strongly depressed by admixture with methyl hemimellitate, m. p. 102°.

Hexadecahydropyrenes.—(*a*) Pyrene (25 g.) in *cyclo*hexane (150 c.c.) was hydrogenated with Raney nickel (10 g.) at 100° for 6½ hours (initial press., 135 atm.). The product was a colourless liquid, b. p. 171—173°/12 mm. (26 g.) (Found: C, 88·3; H, 11·75. $C_{16}H_{26}$ requires C, 88·0; H, 12·0%). (*b*) In another hydrogenation carried out at 150—160° for 5 hours (initial press., 145 atm.) the product was a liquid, b. p. 315—324°, which partly crystallised. The crystals were drained, and recrystallised from alcohol (1·6 g. from 25 g. of pyrene). The m. p. was 90—91°. This substance did not absorb hydrogen when its ethanolic solution was shaken with hydrogen and Adams's platinum catalyst. For purification, its solution in hexane was shaken with concentrated sulphuric acid. *Hexadecahydropyrene* (III), recovered from the washed hexane solution, separated from ethanol in small, colourless, prismatic needles, m. p. 90—91° (Found: C, 88·15, 87·9; H, 12·0, 11·9. $C_{16}H_{26}$ requires C, 88·0; H, 12·0%).

9 : 10-*Dihydroanthracene.*—Anthracene (25 g.) in ethanol (250 c.c.) was hydrogenated over copper chromite (5 g.) at 100° for 6 hours (initial press., 160 atm.). The resulting 9 : 10-dihydroanthracene (22·5 g.) crystallised in colourless needles, m. p. 109—110°.

1-(o-*Carboxybenzoyl*)-s-*hexahydropyrene.*—Powdered anhydrous aluminium chloride (7·5 g.) was added gradually to a stirred mixture of *s*-hexahydropyrene (10 g.), phthalic anhydride (7·5 g.), and benzene (60 c.c.). Stirring was continued at room temperature for 6 hours, the product decomposed with ice and hydrochloric acid, and the benzene removed in steam. The solid in suspension was collected, extracted with hot dilute sodium carbonate solution, and the extract filtered from unreacted hexahydropyrene (5·1 g.). Acidification of the filtrate precipitated 1-(o-*carboxybenzoyl*)-s-*hexahydropyrene* (8·7 g.), which crystallised from benzene (charcoal) in almost colourless needles, m. p. 176·5—178° (Found: C, 81·0; H, 5·5. $C_{24}H_{20}O_3$ requires C, 80·9; H, 5·6%). Treatment with concentrated sulphuric acid at 65° led to sulphonation.

1-(o-*Carboxybenzyl*)-s-*hexahydropyrene* (VI).—A solution of the keto-acid (2·4 g.) in water (25 c.c.) containing sodium hydroxide (2 g.) was boiled under reflux for 44 hours with zinc dust (5 g.) activated with copper (much lactone was obtained if the period of boiling was curtailed). The filtered solution was acidified with hydrochloric acid and the suspension was boiled for a few minutes to ensure lactonisation of some hydroxy-acid. The reduced *acid* (VI), extracted from the precipitate by sodium carbonate solution and reprecipitated by hydrochloric acid, formed fine colourless needles (2·1 g.) (from benzene), m. p. 215—216° (Found: C, 84·3; H, 6·5. $C_{24}H_{22}O_2$ requires C, 84·2; H, 6·4%).

1 : 1′-4 : 4′-*Bis*(*trimethylene*)-2 : 3-*benz*-10-*anthrone* (VII).—The foregoing acid (1·3 g.) was heated for an hour in an oil-bath at 140—150° with acetic anhydride (5·5 c.c.), acetic acid (10 c.c.), and zinc chloride (0·1 g.). The orange crystals which separated on cooling were collected and washed with ethanol. The *ketone* (VII) (1·1 g.) formed fine orange needles (from benzene–ethanol), m. p. 167—168° (Found: C, 89·1; H, 6·2. $C_{24}H_{20}O$ requires C, 88·9; H, 6·2%). The colour of an alcoholic solution was not deepened by addition of alkali (compare Fieser, *loc. cit.*) and there was no indication of salt formation. Oxidation with sodium dichromate in boiling acetic acid gave an amorphous brown solid which could not be crystallised.

Our thanks are due to the Carnegie Trust of the Universities of Scotland for the award of a Scholarship (to W. G.) and also for a grant for the purchase of an autoclave in which the hydrogenation experiments were performed. We are also indebted to Imperial Chemical Industries Ltd. (Dyestuffs Division) for a gift of pyrene.

UNIVERSITY OF GLASGOW. [*Received, December 28th,* 1944.]