

16. A New Synthetic Route to Hydroaromatic Ketones related to Anthracene and Phenanthrene.

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THE objects of this investigation were (a) the preparation of stereochemically homogeneous polycyclic hydroaromatic compounds which might serve as a starting point in a study of the stereochemistry of completely hydrogenated polycyclic systems, and (b) the exploitation of new methods of synthesis of compounds derived from the carcinogenic hydrocarbon 3:4-benzphenanthrene. The latter project was checked by the unforeseen chemical behaviour of 2-(1'-naphthyl)cyclohexanol, and we report now only the preparation of this carbinol, the properties of which are being further examined.

As a starting point in our study of the stereochemistry of perhydrophenanthrene derivatives we required the hexahydrophenanthrone (V), which should exist in two racemic forms (*cis* and *trans* with reference to the points of fusion of the two reduced rings). A method has been devised whereby one of these forms may be obtained readily in moderate amount. The other form has been isolated as a by-product, and it may be possible to modify the stages so that this will become the main product.

Obvious intermediate compounds to use in the synthesis of hexahydrophenanthrone were 2-phenylcyclohexanol and 2-phenylcyclohexanone, but published methods of preparation of these substances (see, for example, von Braun, Gruber, and Kirschbaum, *Ber.*, 1922, **55**, 3670; Brazidec, *Bull. Soc. chim.*, 1915, **17**, 104; Lévy and Sifras, *Compt. rend.*, 1928, **187**, 45) were inconvenient for our purpose. By the action of phenylmagnesium bromide on cyclohexene oxide Bedos (*Bull. Soc. chim.*, 1926, **39**, 292) obtained a very poor yield of impure 2-phenylcyclohexanol. The reason for this bad result is evident from subsequent investigations on the action of Grignard reagents on cyclohexene oxides and 2-chlorocyclohexanols, the normal consequence of these reactions being contraction of the

ring with the formation of *cyclopentylcarbinols* (Vavon and Mitchovitch, *Compt. rend.*, 1928, **186**, 702; Bedos, *ibid.*, 1929, **189**, 255; contrast Godchot and Bedos, *ibid.*, 1924, **178**, 1184). The presence of magnesium halide is a factor in promoting these rearrangements, for *cyclohexene oxide* can be transformed into *cyclopentylformaldehyde* by ethereal magnesium bromide (Bedos, *loc. cit.*; compare Arbusow, *Ber.*, 1935, **68**, 1434). Moreover, Bartlett and Berry (*J. Amer. Chem. Soc.*, 1934, **56**, 2683) have shown that ring contraction can be avoided, and the normal substituted *cyclohexanols* obtained, by the use of halide-free magnesium alkyls. From these and other cognate investigations (Henry, *Compt. rend.*, 1907, **145**, 21; Godchot and Cauquil, *ibid.*, 1928, **186**, 375, 955; Tiffeneau and Tchoubar, *ibid.*, 1934, **198**, 941; Vavon and collaborators, *Bull. Soc. chim.*, 1929, **45**, 965; 1930, **47**, 904; 1932, **51**, 994) it seems that rearrangement occurs when the second stage of the interaction between the Grignard reagent and the oxide or chlorohydrin is brought about by heating the intermediate compound, after distillation of the ether (compare Grignard, *Compt. rend.*, 1903, **136**, 1260; 1905, **141**, 44; *Ann. Chim.*, 1907, **10**, 23).

We have re-examined the reaction between phenylmagnesium bromide and *cyclohexene oxide*. The usual phenomena were observed. A precipitate of the intermediate compound was rapidly formed, which gave apparently 2-bromocyclohexanol when decomposed with water, whereas a violent reaction set in when this intermediate compound was heated on the water-bath. The violence could be moderated by the use of anisole as a solvent, but the carbinol fraction subsequently isolated gave no crystalline dinitrobenzoate, and no crystalline semicarbazone could be obtained from the chromic acid oxidation product. Evidently rearrangement to phenylcyclopentylcarbinol (Edwards and Reid, *J. Amer. Chem. Soc.*, 1930, **52**, 3236) had taken place to a considerable extent. This rearrangement was completely avoided, and 2-phenylcyclohexanol was obtained in almost quantitative yield, when phenyl-lithium was substituted for phenylmagnesium bromide. 2-(1'-Naphthyl)cyclohexanol was likewise obtained from 1-naphthyl-lithium and *cyclohexene oxide*. These results corroborate the conclusions of Bartlett and Berry (*loc. cit.*) that the presence of halide is necessary for the molecular rearrangements which occur under the influence of Grignard reagents.

We have also examined the action of benzylmagnesium chloride on 2-chlorocyclohexanol and *cyclohexene oxide*, with rather remarkable results. In the former case the usual two-stage reaction occurred, attended by complete rearrangement. The resulting carbinol was oxidised to a ketone which differed from the known 2-benzylcyclohexanone, and hence by analogy the carbinol is represented by formula (I). The Grignard reagent



from benzyl chloride reacted readily with *cyclohexene oxide* with liberation of heat, the phenomena being parallel to those observed in the reactions with aryl-lithiums. Hence it seemed likely that complete reaction, and not merely the first stage, had taken place. This proved to be the case, for decomposition with water gave a 50% yield of 2-benzylcyclohexanol (II), identical with that prepared by a method which establishes its structure (Cook and Hewett, this vol., p. 69). The only analogous case in the recent literature, of condensation between a Grignard reagent and *cyclohexene oxide* without rearrangement, is given by Fulton and Robinson (*J.*, 1933, 1463), who believed that they had obtained 2-β-phenylethylcyclohexanol with β-phenylethylmagnesium bromide. However, the experimental description given by these authors is typical of a reaction which is accompanied by rearrangement. Professor Robinson has kindly undertaken a re-investigation of this example, with results which are reported on p. 80.

The abnormal behaviour of benzylmagnesium chloride cannot be ascribed to the equilibrium



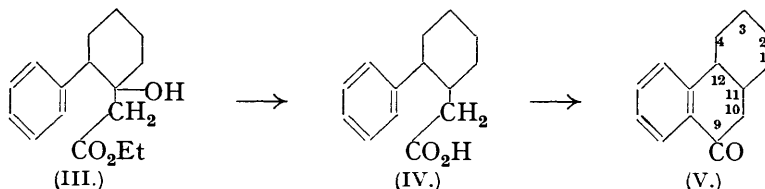
being predominantly in favour of dibenzylmagnesium as, although this is the case, the following figures, quoted from Johnson and Adkins (*J. Amer. Chem. Soc.*, 1932, **54**, 1944;

compare Schlenk, *Ber.*, 1931, **64**, 734), show that the position of equilibrium is much the same with all three compounds under discussion :

Halide.	Yield of Grignard reagent (%).	% present as R ₂ Mg.
Benzyl chloride	93.6 ± 0.7	73.4 ± 2.5
Bromobenzene	94.7 ± 0.5	75.8 ± 2.7
β-Phenylethyl bromide	91.6 ± 0.1	76.0 ± 2.2

The logical conclusion to be drawn from our results is that with Grignard solutions from Benzyl chloride the dialkylmagnesium is more reactive than the alkylmagnesium halide towards *cyclohexene oxide*, whereas in the other two examples the reverse is the case, disturbance of the equilibrium by combination with the more active component of the Grignard solution being rapidly followed by conversion of the less active into the more active component. That some, at any rate, of the Grignard reagent from benzyl chloride reacted in the form of benzylmagnesium chloride was shown by the isolation of a fraction corresponding with 2-chlorocyclohexanol in 20% yield. From the work of Bartlett and Rosenwald (*J. Amer. Chem. Soc.*, 1934, **56**, 1990) this should be the *cis*-compound, and this was probably largely true, as, although a small amount of the phenylurethane of ordinary (*trans*) 2-chlorocyclohexanol was isolated, there was obtained a much larger quantity of a lower-melting phenylurethane, not isolated in the pure state.

For the synthesis of *hexahydrophenanthrone*, 2-phenylcyclohexanol was oxidised to 2-phenylcyclohexanone, which was then condensed with ethyl bromoacetate by the Reformatsky reaction, to give *ethyl 2-phenylcyclohexanol-1-acetate* (III). This was dehydrated to the corresponding unsaturated *ester*, which, after hydrolysis, was hydrogenated to 2-phenylcyclohexylacetic acid (IV), the latter being rapidly dehydrated by concentrated sulphuric acid to 9-keto-1:2:3:4:9:10:11:12-octahydrophenanthrene (hexahydrophenanthrone, V). This ketone could not be obtained crystalline, but gave crystalline derivatives.



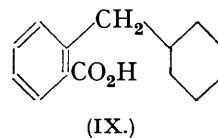
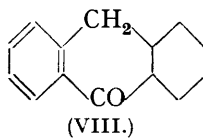
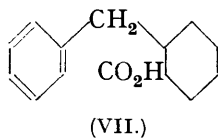
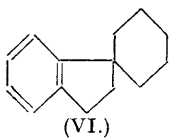
When 2-phenylcyclohexanol was treated with phosphorus tribromide, and the product (obtained in poor yield) condensed with ethyl potassiummalonate, followed by hydrolysis and decarboxylation, there was obtained a small amount of an *acid*, probably stereoisomeric with (IV). The same acid was doubtless present in the lower-melting fractions from the mother-liquors of the crystallisation of (IV), but could not be isolated in the pure state. However, cyclisation of this mixture gave a product, from which a crystalline *isomeride* of (V) was isolated. We are engaged in a determination of the configurations of the two tricyclic ketones (V).

The non-crystalline hexahydrophenanthrone (V) was hydrogenated to a crystalline *octahydro-9-phenanthrol*, which was dehydrogenated by platinum-black at 300° to 9-phenanthrol, and was dehydrated to *hexahydrophenanthrene*, which in its turn was dehydrogenated to phenanthrene.

Although there can be little doubt that the hydrocarbon resulting from cyclisation of β-phenylethyl-Δ¹-cyclohexene is mainly *as*-octahydrophenanthrene (Cook and Hewett, *J.*, 1933, 1108), the evidence of its structure depends upon dehydrogenation of the hydrocarbon or of its derivatives (Cook and Haslewood, *J.*, 1935, 767) to completely aromatic compounds of established structure. Independent confirmation has now been afforded by oxidation of this hydrocarbon to the ketone (V), identical with the non-crystalline ketone prepared from 2-phenylcyclohexanone. By fractional crystallisation of the oximes there were obtained not only the *oxime*, m. p. 124°, of (V), but also an *oxime*, m. p. 187°, which was not the oxime of the stereoisomeric ketone (V). This new oxime is possibly that of a ketone derived from the spirocyclic hydrocarbon (VI), the presence of which would be

expected in the hydrocarbon mixture used for oxidation, although the analytical data for the oxime, m.p. 187°, are in much better agreement with a compound containing two hydrogen atoms less.

Conversion of 2-benzylcyclohexanol into the corresponding 1-chloro-2-benzylcyclohexane was attended by partial dehydration, so that the chloro-compound was contaminated with hydrocarbon. When carbon dioxide was passed into a Grignard solution prepared from this crude chloro-compound, a mixture of the two stereoisomeric 2-benzylhexahydrobenzoic acids (VII) resulted. The partial Walden inversion had probably occurred in the preparation of the chloro-compound. The higher-melting acid (134°), obtained more readily by reduction of *o*-benzylbenzoic acid by sodium and amyl alcohol, was rapidly dehydrated by concentrated sulphuric acid to a mixture of hexahydroanthrones (VIII). The more abundant constituent, m. p. 109°, was also obtained by an internal Friedel-Crafts reaction with the acid, m. p. 134°.



The lower-melting 2-benzylhexahydrobenzoic acid (86—88°), not obtained completely pure, was also dehydrated to a mixture of the hexahydroanthrone, m. p. 109°, and a larger proportion of the more soluble isomeride, m. p. 80°. The formation of both hexahydroanthrones in these reactions evidently involves interconversion of the ketones through an intermediate enolic form, as in the transformation of *cis*- α -decalone into *trans*- α -decalone (Hückel, *Annalen*, 1925, 441, 31), and of 3 : 6-diketocholanic acid into the *allo*-compound (Windaus and Bohne, *Annalen*, 1923, 433, 278; Windaus, *ibid.*, 1926, 447, 244). The two stereoisomeric hexahydroanthrones were characterised by their sharp-melting oximes, and anthracene and anthraquinone were obtained from both of them by dehydrogenation, and then oxidation. The isolation of two oximes is of interest, as Hückel (*loc. cit.*) has shown that *cis*- and *trans*- α -decalones both give the same oxime. We are seeking experimental proof that the hexahydroanthrone, m. p. 109°, is the *trans*-compound.

On account of the large amount of hydrocarbon formed in the conversion of 2-benzylcyclohexanol into its chloride, the bromide was substituted in a succeeding experiment. This was obtained in 44% yield by means of phosphorus tribromide, and in the hope of improving the yield in the next stage, ethyl chloroformate was substituted for carbon dioxide in the Grignard condensation. No better yield was obtained. The esters formed in the reaction were hydrolysed, and the mixture of acids was separated by fractional crystallisation into *trans*-2-benzylhexahydrobenzoic acid, m. p. 134°, and a third isomeride, m. p. 140°. None of the *cis*-acid was apparently formed. Stereochemical theory cannot easily accommodate a third acid of structure (VII). The new acid, m. p. 140°, which was completely sulphonated by brief treatment with concentrated sulphuric acid, may be 4-benzylhexahydrobenzoic acid, formed by migration of bromine in the intermediate bromo-compound (compare Nenitzescu and Gavăt, *Annalen*, 1935, 519, 260). Experiments to test this hypothesis are in progress.

o-Benzylbenzoic acid was readily hydrogenated at ordinary pressure by Adams's platinum oxide catalyst to a hexahydro-acid, m. p. 96°, different from all three hexahydroacids already mentioned. This was saturated, and was unattacked by cold concentrated sulphuric acid, and was therefore ω -cyclohexyl-*o*-toluic acid (IX). Confirmation of this was afforded by oxidation by alkaline permanganate to phthalic acid. It is remarkable that chemical reduction should attack the carboxylated ring of *o*-benzylbenzoic acid, whereas catalytic hydrogenation attacks the other ring. An analogous case is *o*-phenylbenzoic acid, which behaves in the same way (Cook and Hewett, this vol., p. 65).

EXPERIMENTAL.

Carbinols from 2-Chlorocyclohexanol and cycloHexene Oxide.—The materials used in these experiments were prepared by Mr. F. Goulden by the procedure given in "Organic Syntheses" (Collective Vol. I, pp. 151, 179).

Benzylcyclopentylcarbinol (I). 2-Chlorocyclohexanol (10 g.) was added to an ice-cold Grignard reagent prepared from benzyl chloride (19 g.), magnesium turnings (3.6 g.), and anhydrous ether (100 c.c.). After being kept 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 by shaking with ether and ammonium chloride solution, and the ethereal extract was washed, dried, and distilled. The carbinol (7.7 g.) formed a viscous liquid, b. p. 166—169°/20 mm., which crystallised when strongly cooled. The 3 : 5-dinitrobenzoate, prepared by heating a mixture of this carbinol (4 g.) with 3 : 5-dinitrobenzoyl chloride (6 g.) in pure pyridine (20 c.c.) at 100° for $\frac{1}{4}$ hour, crystallised from alcohol in thin colourless needles, m. p. 100.5—101.5° (Found : C, 62.3; H, 5.4. $C_{20}H_{20}O_6N_2$ requires C, 62.5; H, 5.25%). Hydrolysis of this ester with boiling aqueous-alcoholic potash gave pure *benzylcyclopentylcarbinol* (I), which was distilled at 0.1 mm. from a bath at 120°. The colourless distillate crystallised on standing, and had m. p. 30° (Found : C, 81.7; H, 9.65. $C_{13}H_{18}O$ requires C, 82.0; H, 9.5%). For oxidation to the ketone, a solution of chromic acid (0.4 g.) in 80% acetic acid (1.5 c.c.) was added dropwise to a solution of the carbinol (0.7 g.) in glacial acetic acid (10 c.c.), and the whole was kept at room temperature over-night. The oxidation product was isolated and treated with semicarbazide hydrochloride and sodium acetate in boiling aqueous-alcoholic solution. The *semicarbazone* of phenylacetylcyclopentane crystallised from alcohol in colourless needles, m. p. 117—118° (Found : N, 17.4. $C_{14}H_{19}ON_3$ requires N, 17.1%).

2-*Benzylcyclohexanol* (II). *cyclo*Hexene oxide (35 g.) was slowly added to an ice-cold Grignard reagent prepared from benzyl chloride (47.5 c.c.), magnesium turnings (10.5 g.), and anhydrous ether (250 c.c.). After removal of the flask from the ice-bath, the solution boiled spontaneously, and continued to boil for a while. When the reaction had subsided, the whole was refluxed for an hour, and the product decomposed with ammonium chloride solution. The washed ethereal solution was dried and distilled. The lower fractions were redistilled, and gave a fraction, b. p. 85—95°/25 mm. (10 g.), which appeared to be a mixture of stereoisomeric 2-chlorocyclohexanols (see below). The carbinol fraction, b. p. 130°/5—6 mm., was recrystallised from ligroin, giving long colourless needles of 2-benzylcyclohexanol (34 g.), m. p. 76.5—77.5°, alone or mixed with a specimen prepared by reduction of 2-benzylcyclohexanone (Cook and Hewett, this vol., p. 69). The 3 : 5-dinitrobenzoate of 2-benzylcyclohexanol crystallised from alcohol in pale yellow, stout needles, m. p. 133—135° (Found : C, 62.4; H, 5.4. $C_{20}H_{20}O_6N_2$ requires C, 62.5; H, 5.25%). Oxidation of 2-benzylcyclohexanol with cold chromic acid, as described above, gave in good yield 2-benzylcyclohexanone, the semicarbazone of which had m. p. 168—169° alone or mixed with a specimen prepared from α -benzylpimelic acid (Cook and Hewett, *loc. cit.*).

2-*Chlorocyclohexanol*. The fraction, b. p. 85—95°/25 mm., from the above preparation of 2-benzylcyclohexanol was treated with phenyl isocyanate in light petroleum. After some days a heavy oil separated which slowly deposited crystals. These, recrystallised successively from alcohol and cyclohexane (some carbanilide remained undissolved), had m. p. 89—90°, not depressed by a specimen of the phenylurethane of *trans*-2-chlorocyclohexanol, m. p. 94—96° (Godchot, *Compt. rend.*, 1923, 176, 448, gives m. p. 97—98°). The major portion of the phenylurethane was present in the non-crystalline fraction. This was distilled at 0.1 mm. (b. p. about 170°), and crystallised from ligroin, and then from cyclohexane. The product, probably mainly the phenylurethane of *cis*-2-chlorocyclohexanol, formed colourless crystals, m. p. 56—59° to a cloudy liquid. Contamination with a little of the higher-melting compound rendered complete purification impracticable.

2-*Phenylcyclohexanol*. *cyclo*Hexene oxide (49 g.) was added to an ice-cold solution of phenyl-lithium prepared from bromobenzene (50 c.c.), stout lithium wire (7.5 g.), and anhydrous ether (500 c.c.), the whole operation being conducted in an atmosphere of nitrogen (compare Gilman, Zoellner, and Selby, *J. Amer. Chem. Soc.*, 1932, 54, 1957). After removal from the ice-bath, the solution boiled spontaneously for $\frac{1}{2}$ hour. Boiling was continued for 2 $\frac{1}{2}$ hours, and the whole was then kept at room temperature over-night, and decomposed with ice-water. Distillation gave a fraction, b. p. 60—80°/16 mm. (15 g.; mainly cyclohexene oxide), and then 2-phenylcyclohexanol (63.3 g.), b. p. 153—154°/16 mm. This carbinol had m. p. 56—57° after crystallisation from light petroleum, and gave a phenylurethane, m. p. 137—138.5° (von Braun, Gruber, and Kirschbaum, *loc. cit.*, give 54—55°, and 138—139°, as the m. p.'s of 2-phenylcyclohexanol and its phenylurethane). The 3 : 5-dinitrobenzoate of 2-phenylcyclohexanol had m. p. 121—121.5° (from alcohol) (Found : C, 61.5; H, 4.9. $C_{19}H_{18}O_6N_2$ requires C, 61.6; H, 4.9%). Additional proof of the structure of the carbinol was afforded by its oxidation products (below).

2-(1'-Naphthyl)cyclohexanol. *cyclo*Hexene oxide (49 g.) was slowly added to an ice-cold solution of 1-naphthyl-lithium prepared from 1-bromonaphthalene (103.5 g.), stout lithium wire (7.5 g.), and anhydrous ether (500 c.c.), the operations being conducted in an atmosphere of nitrogen. After addition of the oxide, the solution was kept in ice for $\frac{1}{2}$ hour, then at room temperature for 1 hour, and was finally boiled for 15 hours. After decomposition with ice, the ethereal solution was washed, dried (sodium sulphate), and distilled. The carbinol fraction was redistilled, and the crystalline distillate (47.5 g., b. p. 183°/1 mm.) was recrystallised from alcohol. 2-(1'-Naphthyl)cyclohexanol formed colourless microscopic plates, m. p. 129—130° (Found: C, 84.7; H, 7.75. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%). Its 3:5-dinitrobenzoate formed a primrose-yellow microcrystalline powder (from alcohol), m. p. 162—163° (Found: C, 65.6; H, 4.95. $C_{23}H_{20}O_6N_2$ requires C, 65.7; H, 4.8%), and its *phenylurethane* crystallised from *cyclohexane* in colourless microscopic needles, m. p. 134—135° (Found: C, 79.3; H, 6.7. $C_{23}H_{25}O_2N$ requires C, 79.95; H, 6.7%).

The structure of this carbinol was established by its dehydration to 1-naphthyl- Δ^1 -cyclohexene, identical with a specimen prepared from 1-(1'-naphthyl)cyclohexanol (Weiss and Woidich, *Monatsh.*, 1925, 46, 456): A mixture of the carbinol (3 g.) and anhydrous zinc chloride (6 g.) was heated at 160—170° for 40 minutes, cooled, and extracted with benzene, and the benzene extract distilled. The distillate, b. p. 131°/0.4 mm., which absorbed a quantity of bromine corresponding with one double bond, was converted into the picrate, and this was recrystallised several times from methyl alcohol (m. p. 120—121.5°). The hydrocarbon regenerated from this picrate was distilled over sodium in a vacuum, and recrystallised from methyl alcohol; it then had m. p. 44°, not depressed by an authentic sample of 1'-naphthyl- Δ^1 -cyclohexene. Weiss and Woidich give m. p. 36° for this hydrocarbon, but our sample, prepared by their method, had m. p. 46° after crystallisation from methyl alcohol, and gave a picrate, m. p. 124.5—125.5°.

The same hydrocarbon resulted from an attempt to prepare the bromide by adding phosphorus tribromide (10 g.) during 20 minutes to a suspension of 2-(1'-naphthyl)cyclohexanol (24.4 g.) in carbon tetrachloride (25 c.c.), cooled in a freezing mixture. After being kept at room temperature over-night, the reaction mixture was decomposed with water, and the carbon tetrachloride solution was washed and distilled. The product, b. p. 166°/0.3 mm. (12 g.), contained some unaltered carbinol, which separated when a solution in light petroleum was cooled in a freezing mixture. The redistilled hydrocarbon (Found: C, 90.7; H, 7.9%) was purified through its picrate and crystallised from methyl alcohol; it then had m. p. 44°, not depressed by an authentic specimen of the *cyclohexene*.

Hydrophenanthrene Derivatives.—2-Phenylcyclohexanone. A solution of chromic acid (33 g.) in 80% acetic acid (65 c.c.) was added dropwise to a stirred solution of 2-phenylcyclohexanol (56.5 g.) in glacial acetic acid (625 c.c.). After being kept at room temperature over-night, the acetic acid was removed in a vacuum, and the residue extracted with water and ether. The ethereal extract was washed with sodium carbonate solution, giving 9.6 g. of δ -benzoylevaleric acid, m. p. 75—76° (from *cyclohexane*) (Found: C, 69.8; H, 6.9. Calc.: C, 69.9; H, 6.8%). The semicarbazone had m. p. 183—185° (Auwers and Treppmann, *Ber.*, 1915, 48, 1217, give 77—78° and 187°, as the m. p.'s of this acid and its semicarbazone).

The neutral ethereal solution of the oxidation products was dried and distilled, yielding 32.7 g. of 2-phenylcyclohexanone (b. p. 160°/16 mm.). This ketone had m. p. 50—53° after crystallisation from light petroleum, and gave an oxime and a semicarbazone having the m. p.'s recorded by von Braun, Gruber, and Kirschbaum (*loc. cit.*).

Ethyl 2-phenylcyclohexanol-1-acetate (III). A mixture of 2-phenylcyclohexanone (32.7 g.), ethyl bromoacetate (33.6 g.), dry zinc filings (purified by washing first with warm alkali and then with alcohol and ether; 13.6 g.), and pure benzene (100 c.c.) was warmed on the water-bath until a reaction set in. The vigorous reaction caused the mixture to boil for 10 minutes without external heating. When this had subsided, the whole was boiled for $\frac{1}{2}$ hour, and the product decomposed with ice-cold dilute sulphuric acid, washed, dried, and distilled. The *hydroxy-ester* (III) (34 g., 70% yield) had b. p. 146—154°/0.8 mm., and was shown by analysis to have undergone partial dehydration (Found: C, 75.4; H, 8.4. $C_{16}H_{22}O_3$ requires C, 73.25; H, 8.5%). The *hydroxy-acid* (corresponding with III) was obtained by hydrolysis, and crystallised from water in small colourless needles, m. p. 128—129° (Found: C, 71.5; H, 7.6. $C_{14}H_{18}O_3$ requires C, 71.7; H, 7.8%).

Ethyl 2-phenyl- Δ^1 -cyclohexenylacetate. Thionyl chloride (16.9 g.) was added slowly to a well-stirred ice-cold mixture of the foregoing hydroxy-ester (34 g.), anhydrous ether (60 c.c.), and pure pyridine (28.6 c.c.). Stirring and cooling were continued for 2 hours, the solution was

then poured into water, and the ethereal solution was washed, dried, and distilled. *Ethyl 2-phenyl- Δ^1 -cyclohexenylacetate* (27.4 g.) formed a colourless liquid, b. p. 123—125°/0.8 mm. (Found: C, 78.2; H, 8.2. $C_{16}H_{20}O_2$ requires C, 78.6; H, 8.3%). Hydrolysis with boiling aqueous-alcoholic potash gave *2-phenyl- Δ^1 -cyclohexenylacetic acid*, a gum, b. p. 150—155°/0.4 mm., which slowly crystallised. After crystallisation from ligroin this acid formed colourless rhombs, m. p. 92.5—93.5° (Found: C, 78.1; H, 7.6. $C_{14}H_{16}O_2$ requires C, 77.7; H, 7.5%).

2-Phenylcyclohexylacetic Acid (IV). The distilled, but not recrystallised, unsaturated acid (17.5 g.) was hydrogenated in acetic acid solution, a palladium-black catalyst being used. The resulting *2-phenylcyclohexylacetic acid* (12.4 g.) crystallised from aqueous acetic acid in conglomerates of colourless needles, m. p. 168—170° (Found: C, 76.9; H, 8.3. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%). The liquors contained a lower-melting acid, but this could not be isolated in the pure state. When, however, a fraction, m. p. 65—85° (about 2 g.), was dehydrated with concentrated sulphuric acid (20 c.c.) at 100°, and the product crystallised from light petroleum, there was formed a *ketone* (0.5 g.), m. p. 95—96° (Found: C, 84.0; H, 8.1. $C_{14}H_{16}O$ requires C, 83.95; H, 8.1%), which gave an *oxime*, m. p. 175—177° (Found: C, 78.6; H, 7.9. $C_{14}H_{17}ON$ requires C, 78.1; H, 8.0%). This ketone is probably stereoisomeric with the hexahydrophenanthrone (V) obtained by dehydration of the above acid of m. p. 168—170°.

Stereoisomeric 2-phenylcyclohexylacetic acid (?).^{*} A solution of *2-phenylcyclohexanol* (17.6 g.) in carbon tetrachloride (25 c.c.) was added during 2 hours with stirring to phosphorus tribromide (13.6 g.), cooled in a freezing mixture. The mixture was stirred at 15° for another hour, and the bromo-compound, b. p. 150—155°/16 mm. (4.8 g.), was isolated in the usual way. This was added to the potassio-compound from ethyl malonate (7.2 g.) and potassium (1.2 g.) in benzene (15 c.c.), and the whole was heated on the water-bath for 4 days. The product was decomposed with water, and the benzene solution dried and distilled. The fraction, b. p. 120—150°/1 mm. (3.1 g.), was hydrolysed with aqueous-alcoholic potash, the acidic product heated at 200° in order to effect decarboxylation of the substituted malonic acid, and the resulting *2-phenylcyclohexylacetic acid* crystallised from water. It formed small colourless plates, m. p. 84—85°. The yield was only 0.1 g. (Found: C, 77.1; H, 8.3. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%).

9-Keto-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (hexahydrophenanthrone) (V). (a) A mixture of *2-phenylcyclohexylacetic acid* (m. p. 168—170°) (1.5 g.) and thionyl chloride (5 c.c.) was refluxed for an hour, the excess of thionyl chloride removed in a vacuum, and the residual acid chloride dissolved in carbon disulphide (7.5 c.c.) and treated at 0° with anhydrous aluminium chloride (1 g.). After being kept in the ice-bath for $\frac{1}{4}$ hour, the whole was heated to boiling and then decomposed with ice and hydrochloric acid. The ketone (0.8 g.), b. p. 132—135°/0.5 mm., was identical with that obtained by dehydration with sulphuric acid.

(b) A solution of *2-phenylcyclohexylacetic acid* (9.5 g.) in concentrated sulphuric acid (47.5 c.c.) was heated on the water-bath for 10 minutes, cooled, and poured on ice. The ketone was extracted with ether, washed with dilute sodium carbonate solution, and distilled. *9-Keto-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene* (6.3 g.) formed a colourless syrup, b. p. 137—138°/0.5 mm. (Found: C, 83.8; H, 8.0. $C_{14}H_{16}O$ requires C, 83.95; H, 8.1%). The *semicarbazone* formed a colourless crystalline powder (from alcohol), m. p. 195—196° (Found: C, 70.5; H, 7.4. $C_{15}H_{18}ON_3$ requires C, 70.3; H, 7.1%), and the *oxime*, obtained by 3 hours' heating at 100° with hydroxylamine hydrochloride in anhydrous pyridine, crystallised from methyl alcohol in colourless needles, m. p. 123.5—124.5° (Found: C, 77.75; H, 8.1. $C_{14}H_{17}ON$ requires C, 78.1; H, 8.0%).

9-Hydroxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene. A solution of the ketone (V) (4 g.) in ethyl alcohol (40 c.c.) was hydrogenated, Adams's platinum oxide catalyst (0.5 g.) being used. The resulting *carbinol* was crystallised from cyclohexane and then light petroleum, forming soft colourless needles (2.6 g.), m. p. 114—115° (Found: C, 82.8; H, 8.75. $C_{14}H_{18}O$ requires C, 83.1; H, 9.0%). Dehydrogenation with platinum-black at 310—320° (4 hours) gave 9-phenanthrol, m. p. 151—152° (*lit.*, 152°) after purification through its picrate, m. p. 182—184° (*lit.*, 183°). A more soluble picrate, probably of phenanthrene, was also present in the crude product.

Hexahydrophenanthrene. Octahydrophenanthrol (2.5 g.) was heated at 180° for 20 minutes with anhydrous zinc chloride (5 g.), and the resulting *hexahydrophenanthrene* (1.5 g.) distilled over sodium. It had b. p. 125—126°/2.5 mm. and $n_D^{14.5}$ 1.5810 (Found: C, 90.95; H, 9.0).

^{*} (Added in proof) The same structure (IV) is ascribed by Ghose (*Science and Culture*, 1935, 1, 299) to an acid, m. p. 69—70°, prepared by another method, with the avowed intention of converting it into a phenanthrene derivative.

$C_{14}H_{16}$ requires C, 91.3; H, 8.7%). Dehydrogenation of this hydrocarbon with platinum-black at 300° (2 hours) gave phenanthrene, identified by mixed m. p.'s of the hydrocarbon and its picrate with authentic specimens.

Oxidation of as.-octahydrophenanthrene. A solution of chromic acid (30 g.) in 80% acetic acid (60 c.c.) was added during an hour to a well-stirred solution of *as.*-octahydrophenanthrene (prepared by aluminium chloride cyclisation of β -phenylethyl- Δ^1 -cyclohexene) (25 g.) in glacial acetic acid (250 c.c.). After 4 days at room temperature, *isopropyl* alcohol was added to destroy excess of chromic acid, and the acetic acid was removed on the water-bath under reduced pressure. The residue was extracted with water and ether, and the ethereal extract was washed successively with dilute sulphuric acid, dilute sodium carbonate solution, and water. The dried solution was fractionated. The highest-boiling fraction (6.8 g.), b. p. $100\text{--}130^{\circ}/0.2$ mm., was treated with Girard's ketonic reagent, and the ketonic products regenerated from the aqueous extract by means of hydrochloric acid (details of procedure as given in J., 1935, 1323). The resulting ketone mixture formed a thick yellowish liquid (4.5 g.), which, after distillation at 0.1 mm., was heated on the water-bath for 3 hours with hydroxylamine hydrochloride (4.4 g.) in anhydrous pyridine (20 c.c.). The resulting mixture of oximes was fractionally crystallised from alcohol, giving a sparingly soluble *oxime* (0.35 g.), which formed long colourless needles, m. p. $186.5\text{--}187.5^{\circ}$, and depressed the m. p. of the oxime, m. p. $175\text{--}177^{\circ}$, of one of the stereoisomeric hexahydrophenanthrones (Found: C, 78.8, 78.5; H, 7.4, 6.95; N, 7.0. $C_{14}H_{15}ON$ requires C, 78.8; H, 7.1; N, 6.6%. $C_{14}H_{17}ON$ requires C, 78.1; H, 8.0; N, 6.5%). The more soluble oxime (1.5 g.) was recrystallised from aqueous alcohol; it then had m. p. $119\text{--}121^{\circ}$, not depressed by the oxime, m. p. 124° , of hexahydrophenanthrone (V). This oxime was hydrolysed, and the ketone converted into its semicarbazone, which had m. p. $191\text{--}196^{\circ}$, not depressed by the semicarbazone, m. p. $195\text{--}196^{\circ}$, of hexahydrophenanthrene.

Hexahydroanthrones.—2-Benzylhexahydrobenzoic acids (VII). (a) Thionyl chloride (11.5 c.c.) was added dropwise to an ice-cold mixture of 2-benzylcyclohexanol (27.7 g.) and dimethylaniline (20 c.c.). The whole was then heated on the water-bath until liberation of sulphur dioxide ceased; water was added and the product was extracted with ether, washed, and distilled, giving a colourless liquid (22.2 g.), b. p. $85\text{--}100^{\circ}/0.2$ mm. (Found: C, 80.35; H, 8.8. $C_{13}H_{17}Cl$ requires C, 74.8; H, 8.2%). This chloro-compound was therefore contaminated with much hydrocarbon, and even worse results were obtained when pyridine was used in place of dimethylaniline.

A Grignard solution was prepared from this chloro-compound (20 g.) and magnesium turnings (2.4 g.) in anhydrous ether (100 c.c.), methylmagnesium iodide being required for activation. Dry carbon dioxide was passed into the ice-cold solution for 3 hours, the product was decomposed with dilute hydrochloric acid, and acidic substances were extracted by sodium carbonate solution. The crude resinous acids (isolated by means of ether) were dissolved in ligroin, and the solution kept in the refrigerator for several hours. 3.6 G. of a colourless powder separated, a further 0.45 g. being obtained by concentrating the mother-liquor and adding light petroleum. By fractional crystallisation from ligroin and light petroleum, this mixture was separated into 2-benzylhexahydrobenzoic acid (VII), m. p. $133\text{--}134^{\circ}$, provisionally denoted as the *trans*-acid, which separated from cyclohexane in colourless microscopic crystals (Found: C, 77.2; H, 8.4. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%), and a *stereoisomeride*, provisionally regarded as *cis*-2-benzylhexahydrobenzoic acid, which separated from light petroleum as a colourless crystalline powder, m. p. $86\text{--}88^{\circ}$, although the resulting cloudy liquid was not completely clear below 94° (Found: C, 77.3; H, 8.2%).

(b) Phosphorus tribromide (5 c.c.) was added dropwise during 20 minutes to an agitated suspension of 2-benzylcyclohexanol (28.5 g.) in carbon tetrachloride (25 c.c.), cooled in a freezing mixture. The mixture was kept in the freezing mixture for an hour and then over-night at room temperature. The resulting 1-bromo-2-benzylcyclohexane (16.5 g.; 44% yield), isolated in the usual manner, formed a colourless refractive liquid, b. p. $120^{\circ}/0.4$ mm. (Found: C, 62.5; H, 7.0. $C_{13}H_{17}Br$ requires C, 61.7; H, 6.8%). 6 G. of carbinol were recovered by hydrolysis of the phosphite esters.

An ice-cold Grignard solution prepared from this bromo-compound (16 g.), magnesium turnings (1.55 g.), and anhydrous ether (80 c.c.) was treated with ethyl chloroformate (6.9 g.), diluted with ether (15 c.c.). After being kept in the ice-bath for $\frac{1}{2}$ hour and then at room temperature over-night, the product was treated with ammonium chloride solution, and the ethereal solution was washed, dried, and distilled. The fraction, b. p. $120\text{--}130^{\circ}/0.2\text{--}0.3$ mm. (6.25 g.), was hydrolysed with boiling aqueous-alcoholic potash, and the resulting mixture of acids was fractionally crystallised from ligroin (fractions I and II) and light petroleum (fraction

III) into three fractions: I, m. p. 133—134° (1.45 g.); II, m. p. 138—140° after sintering (0.55 g.); III, m. p. 102—113° (0.75 g.). Fraction I, after crystallisation, had m. p. 133—134.5°, and was shown to be identical with *trans*-2-benzylhexahydrobenzoic acid (VII). Fraction II crystallised from *cyclohexane* in colourless leaflets, m. p. 140—141°, and depressed the m. p. of the acid from fraction I (Found: C, 77.0; H, 8.3. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%). This acid is provisionally regarded as 4-benzylhexahydrobenzoic acid, formed by migration. Diazomethane gave a methyl ester, m. p. 33°. Fraction III seemed to be a mixture of these two acids, but no pure compound could be isolated. The residue from the distillation of the mixture of esters from the Grignard reaction crystallised from xylene, and then from benzene, in colourless crystals, m. p. 180—181° to a cloudy liquid, clear at 191°. This was apparently 2:2'-*dibenzyl-dicyclohexyl*, probably not stereochemically homogeneous (Found: C, 90.2; H, 9.9. $C_{26}H_{34}$ requires C, 90.1; H, 9.9%).

(c) Sodium (16.6 g.) was gradually added to a boiling solution of *o*-benzylbenzoic acid (Barnett, Cook, and Nixon, J., 1927, 508) (5 g.) in amyl alcohol (200 c.c.). After the sodium had dissolved, the solution was poured into water and the amyl alcohol was removed in steam. Most of the alkali was neutralised, the solution filtered, and the filtrate acidified. The acidic product was dried in ethereal solution and recrystallised from ligroin. The crystals (3.3 g.) had m. p. 121—125°, raised by recrystallisation from *cyclohexane* and then ligroin to 133—134°. This m. p. was not depressed by *trans*-2-benzylhexahydrobenzoic acid prepared from 2-benzyl-*cyclohexanol*. This method of preparation supports the *trans*-configuration.

trans-Hexahydroanthrone (VIII). (a) *trans*-2-Benzylhexahydrobenzoic acid (1.5 g.) was submitted to an internal Friedel-Crafts reaction exactly as in the case of 2-phenyl-*cyclohexyl*-acetic acid (p. 77). After removal of the carbon disulphide, crystallisation from alcohol gave 0.8 g. of *trans*-hexahydroanthrone, which formed colourless prisms, m. p. 109—109.5° (Found: C, 83.9; H, 8.2. $C_{14}H_{16}O$ requires C, 83.95; H, 8.1%). Dehydrogenation of this ketone (0.1 g.) with platinum-black (50 mg.) at 300° gave, after crystallisation from benzene, colourless leaflets, m. p. 205—207°, not depressed by anthracene. Without further purification this was oxidised with sodium dichromate in boiling acetic acid, and gave anthraquinone, identified by mixed m. p., and by the anthraquinol reaction with zinc dust and alkali.

(b) Dehydration of *trans*-2-benzylhexahydrobenzoic acid (0.4 g.) by concentrated sulphuric acid (2 c.c.) at 100° (10 minutes) gave the same hexahydroanthrone (0.25 g.), m. p. 109°. It was subsequently found that heating is unnecessary; as soon as the acid has dissolved in cold concentrated sulphuric acid dehydration is complete. This ketone was hardly affected by hydroxylamine in boiling aqueous-alcoholic solution (2 hours), but gave an *oxime* when heated on the water-bath with hydroxylamine hydrochloride (1 part) in anhydrous pyridine (10 parts) for 4 hours.* The *oxime* separated from *cyclohexane* as a colourless crystalline powder, m. p. 174.5—175.5° (Found: C, 78.1; H, 7.8. $C_{14}H_{17}ON$ requires C, 78.1; H, 8.0%).

cis-Hexahydroanthrone (VIII). (a) A solution of *cis*-2-benzylhexahydrobenzoic acid, m. p. 86—88° (1 g.), in concentrated sulphuric acid (5 c.c.) was heated on the water-bath for 5 minutes. The resulting mixture of ketones (0.9 g.) was fractionally crystallised from alcohol. There was isolated 0.15 g. of the pure *trans*-ketone, m. p. 109°. The more soluble fractions yielded 0.4 g. of *cis*-hexahydroanthrone, which crystallised from aqueous alcohol in colourless needles, m. p. 79—80°. The resulting cloudy liquid became clear only at 85°, so a little of the *trans*-ketone was probably still present (Found: C, 84.0; H, 7.9. $C_{14}H_{16}O$ requires C, 83.95; H, 8.1%). The *oxime* of the *cis*-ketone, prepared by the pyridine method, crystallised from ligroin in clusters of colourless needles, m. p. 150—151° (Found: C, 78.2; H, 7.9. $C_{14}H_{17}ON$ requires C, 78.1; H, 8.0%). Dehydrogenation of *cis*-hexahydroanthrone with platinum-black gave anthracene, m. p. 209—211°, oxidised to anthraquinone, m. p. 275°.

(b) When the crude acid, m. p. 121—125° (5 g.), obtained by reduction of *o*-benzylbenzoic acid with sodium and amyl alcohol, was dehydrated with concentrated sulphuric acid (5 minutes at 100°), and the product recrystallised twice from alcohol, pure *trans*-hexahydroanthrone (1.05 g.), m. p. 109°, was obtained. The liquor from the final crystallisation gave, on dilution with water, 1.05 g. of almost pure *cis*-hexahydroanthrone, m. p. 79—80° (clear at 87°). Evidently a mixture of the two anthrones arises from either *cis*- or *trans*-benzylhexahydrobenzoic acid, and this method appears to furnish the simplest route to both hexahydroanthrones. Only the *trans*-ketone was obtained by dehydration with cold sulphuric acid.

ω -*cyclohexyl-o-toluic acid* (IX). A solution of *o*-benzylbenzoic acid (8 g.) in glacial acetic acid (100 c.c.) was shaken with hydrogen in the presence of Adams's platinum oxide catalyst

* We are indebted to Dr. W. E. Bachmann for bringing to our notice this method of oximation.

(1.2 g.). In 10½ hours 2.6 l. of hydrogen were absorbed, corresponding with 6 atoms. The acetic acid was removed under reduced pressure and the residue was recrystallised from light petroleum; it then had m. p. 88—93°. This product was contaminated with a little *o*-benzylbenzoic acid, and for purification, a solution of the acid (4 g.) in concentrated sulphuric acid (20 c.c.) was kept at room temperature for ½ hour and then poured into water. The precipitate was digested with cold dilute sodium carbonate solution, which dissolved the desired acid, leaving a residue of anthrone. ω -cycloHexyl-*o*-toluic acid (IX) crystallised from light petroleum in colourless plates, m. p. 95.5—96.5°, and did not absorb bromine or reduce cold alkaline permanganate (Found: C, 77.2; H, 8.3. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%).

A 5% solution of potassium permanganate (3.5 g.) was added during 1 hour to a boiling solution of this acid (1 g.) in dilute alkali. The filtered solution was acidified and extracted with ether repeatedly. The ethereal extract was dried, and the ether removed. The residual gum gave a white solid when digested with benzene, and from this, phthalic anhydride (identified by mixed m. p.) was obtained by sublimation under reduced pressure.

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NOTE BY R. ROBINSON.—Dr. Fulton and I are glad to have the opportunity of confirming the view of the course of the reaction between β -phenylethylmagnesium bromide and *cyclohexene oxide* put forward in the present communication (p. 72).

cyclopentylformaldehyde, prepared according to the method of Clemo and Ormston (J., 1933, 362), which is based on that of Bedos (*Compt. rend.*, 1929, 189, 255), reacted with β -phenylethylmagnesium bromide in ethereal solution with formation of β -phenylethylcyclopentylcarbinol in excellent yield. The alcohol had the properties previously attributed to 2- β -phenylethylcyclohexanol (Fulton and Robinson, *loc. cit.*) and it solidified completely in a freezing mixture. Definite identification was effected through the semicarbazone of the related ketone, which had m. p. 157°, alone or mixed with the specimen made in stages from *cyclohexene oxide*. The recognition that the reaction involves rearrangement implicates other substances as follows. The *p*-nitrobenzoate and the chloride are β -phenylethylcyclopentylcarbonyl derivatives; for "2- β -phenylethylcyclohexanone" read β -phenylethyl cyclopentyl ketone; for "2- β -phenylethyl-1-ethylcyclohexanol" read β -phenylethylcyclopentylethylcarbinol.

The hydrocarbons described are of uncertain constitution: the supposed 1:2:3:4:9:10:11:12-octahydrophenanthrene solidified at -11° to -12° and was therefore probably homogeneous; it should be 1-cyclopentylhydrindene, and the formation of phenanthrene on heating with sulphur was due to rearrangement. The supposed 2- β -phenylethyl-1-ethyl- Δ^1 -cyclohexene is now best described as a hydrocarbon, $C_{16}H_{22}$, and the supposed ethyl-octahydrophenanthrene, which gave both phenanthrene and anthracene on heating with sulphur, is now also to be regarded as a hydrocarbon, $C_{16}H_{22}$. Incidentally the apparent clash with the results of Bardhan and Sengupta (J., 1932, 2520) no longer exists.—THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [Received, December 12th, 1935.]