of the *cis-* and *trans*-forms of 9-keto-*as*-octahydrophenanthrene into the corresponding nitro-hexahydrodiphenic acids.

The stereochemical implications of these results are discussed and it is shown that they are in agreement with other, less exact, evidence.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS   RECEIVED APRIL 30, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Stereochemistry of Catalytic Hydrogenation. VI. The Hydrogenation of 9-Phenanthrol and Related Substances and the Identification of Three of the Possible Stereoisomeric Forms of the Perhydrophenanthrene Ring

BY R. P. LINSTEAD, RICHARD R. WHETSTONE AND PHILIP LEVINE

Perhydrophenanthrene can theoretically exist in six (inactive) stereoisomeric modifications.[1] Corresponding to each of four of these hydrocarbons (the *cis-syn-cis*, *trans-syn-trans*, *cis-anti-cis* and *trans-anti-trans* forms), there will be one ketone with the carbonyl group at C_9. Corresponding to each of the other two hydrocarbons (the *cis-syn-trans* and *cis-anti-trans* forms), there will be a pair of C_9 ketones, the additional forms being possible because the carbonyl can lie next to either a *cis-* or a *trans*-junction. All the ketones, and all the hydrocarbons except the *cis-syn-cis* and *trans-syn-trans* isomers, are capable of existence in enantiomorphic forms. Furthermore, each ketone can give rise to a pair of epimeric alcohols, so that eight inactive ketones and sixteen inactive alcohols become possible. The possibilities for the ketones are shown.

I. c.s.c.   II. c.s.t.

III. t.s.c.   IV. t.s.t.

V. c.a.c.   VI. c.a.t.

VII. t.a.c.   VIII. t.a.t.
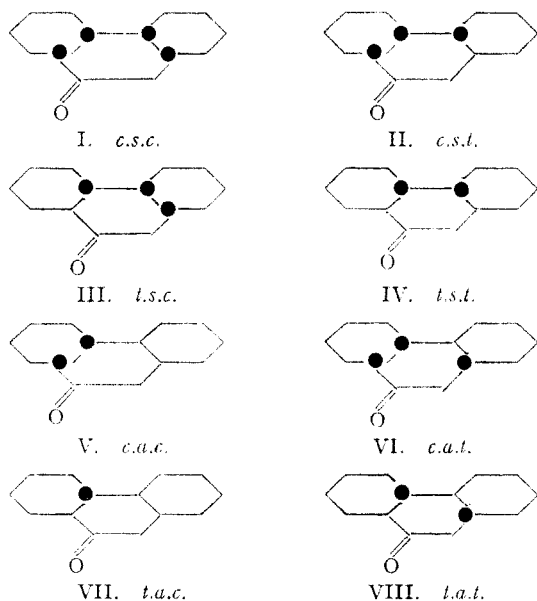
This is parallel to the half esters of the perhydrodiphenic acids[2] and we use a similar convention for the nomenclature of the *cis–trans* forms, the configuration on the side of the ketone group being named first.

It is also convenient for the sake of clarity to use dotted formulas[3] to designate the configuration of the alcohols. Thus of the two possible *cis-syn-*

IX   and   X
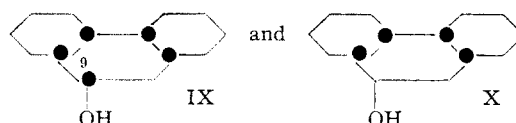
cis alcohols the compound IX has the hydrogen atom on carbon 9 on the same side of the central ring as the four hydrogen atoms at the points of ring fusion.

The first perhydrophenanthrene derivatives of definite configuration to be discovered were the 9-ketone, m. p. 49°, and the related secondary alcohol, m. p. 119°, prepared by Linstead and Walpole.[1] This ketone, a stable crystalline solid, m. p. 49°, was oxidized to a perhydrodiphenic acid of m. p. 244°. This has now been proved to have the *trans-anti-trans* configuration.[4] Hence the ketone has the same configuration (VIII). Two other compounds which were believed[1] to be 9-keto-perhydrophenanthrenes have now been shown[2] to have a different skeleton structure.

In the present paper we describe the preparation of two new stereoisomeric modifications (*cis-syn-cis* and *trans-syn-cis*) of 9-keto-perhydrophenanthrene. Half of the possible stereoisomeric forms of the perhydrophenanthrene ring have therefore been prepared and orientated.
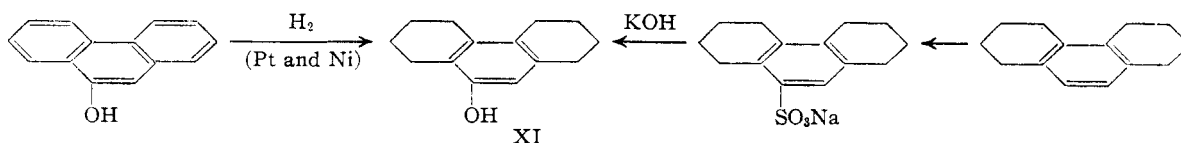
(1) Linstead and Walpole, *J. Chem. Soc.*, 842 (1939).

(2) Linstead and Doering, THIS JOURNAL, **64**, 1991 (1942).

(3) Linstead, *Chemistry and Industry*, **56**, 510 (1937); Linstead and Walpole, *loc. cit.*; Ruzicka, Furter and Goldberg, *Helv. Chim. Acta*, **21**, 498 (1938); Linstead, *et al.*, THIS JOURNAL, **64**, 1985 (1942).

(4) Linstead and Doering, *ibid.*, **64**, 2003 (1942); Linstead, Davis and Whetstone, *ibid.*, **64**, 2009 (1942).

The new isomers were obtained in a study of the catalytic hydrogenation over platinum of 9-phenanthrol and of the *as*-octahydro-9-phenanthrols. Marvel and collaborators[5a,5b] have recently made some observations on the perhydrogenation of 9-phenanthrol over nickel. We shall discuss their results later in this paper.

When 9-phenanthrol was hydrogenated over platinum in acetic acid, there were formed (1) *sym*-octahydro-9-phenanthrol (XI), m. p. 135°, (2) a *cis-syn-cis*-perhydro-9-phenanthrol (IX or X), m. p. 111°, and (3) a hydrocarbon fraction. The *sym*-octahydro compound (which was isolated in very small amount) was identical with material prepared by hydrogenating 9-phenanthrol over Raney nickel. The hydrogenation over a different nickel catalyst has already been carried out by von Braun and Bayer[6] who had obtained the same compound. The structure of *sym*-octahydro-9-phenanthrol was proved by its synthesis from Schroeter's *sym*-octahydrophenanthrene[7] by sulfonation and fusion with alkali. The hydrogenation of 9-phenanthrol over Raney nickel is the best preparative method.

investigated by J. W. Cook and his collaborators[9] were suitable intermediates for such an investigation. These substances were accordingly prepared essentially by Cook's methods. In confirmation of the earlier results,[9a] we found that the dehydration of 2-phenylcyclohexanol-1-acetic ester, followed by hydrolysis, yielded the β,γ-unsaturated acid, m. p. 93° (probably XII), and that catalytic hydrogenation of this gave almost exclusively a 2-phenylcyclohexane-1-acetic acid of m. p. 170°. The evidence which we present below proves the correctness of Cook's view[9b] that this saturated acid has the *cis*-configuration (XIII). 2-Phenylcyclohexane-1-acetic acid can exist in a second geometrical form, and various reports of this have been made. Cook, Hewett and Lawrence[9a] obtained it in an impure form (m. p. 65–85°) from the mother liquors of the *cis*-acid. They also reported an acid of m. p. 84–85° which was obtained in poor yield by a malonic ester synthesis. Ghose[10] has described an acid of m. p. 69–70°, made by a different method. Cook, Hewett and Robinson[9b] reported that 2-phenylcyclohexylideneacetic acid (XIV, made by de-

The main oxygen-containing product of the platinum hydrogenation of 9-phenanthrol was a perhydro alcohol, m. p. 110–111°. This was easily separated from the octahydro-compound as it was lower boiling and more soluble. On oxidation with nitric acid it yielded *cis-syn-cis* perhydrodiphenic acid, m. p. 289°. This at once proved both its structure and its configuration (apart from the orientation of the hydroxyl group at C$_9$). We discuss the chemistry of this alcohol more fully below.

It was observed by Linstead and Davis[8] that in the perhydrogenation of *cis*- and *trans*-hexahydrodiphenic acids over platinum the integrity of the already established configuration was preserved, and the subsequent hydrogenation went *syn*- and *cis*-. It was of great interest to see if the same principle held in the tricyclic series. The *cis*- and *trans*-9-keto-*as*-octahydrophenanthrenes recently

hydrating the hydroxy acid with acetic anhydride) on hydrogenation failed to give the second (*trans-*) saturated acid in useful amount. We can confirm that the α,β-acid (XIV) hydrogenates *cis*- under most conditions. When, however, the hydrogenation is carried out over palladium in benzene solution there is obtained a mixture of saturated acids from which 57% of the *cis*-acid (m. p. 170°) and 33% of an isomer, m. p. 114°,[10a] can be separated without difficulty. The latter is undoubtedly the pure *trans*-2-phenylcyclohexane-1-acetic acid (XV). On cyclization with sulfuric acid, it gives the (*trans-*) 9-keto-*as*-octahydrophenanthrene, m. p. 96°, which Cook[9a] had obtained from his impure acid, m. p. 65–85°. The latter material must therefore have contained the *trans*-acid; the structure of the other low-melting acids described in the literature is doubt-

(5) (a) Marvel and White, THIS JOURNAL, **62**, 2739 (1940); compare (b) Marvel and Patterson, *ibid.*, **63**, 2218 (1941).

(6) von Braun and Bayer, *Ber.*, **58**, 2667 (1925).

(7) Schroeter, *ibid.*, **57**, 1990 (1924).

(8) Linstead and Davis, THIS JOURNAL, **64**, 2006 (1942).

(9) (a) Cook, Hewett and Lawrence, *J. Chem. Soc.*, 71 (1936); (b) Cook, Hewett and Robinson, *ibid.*, 168 (1939).

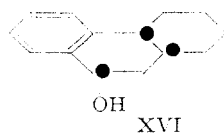(10) Ghose, *Science and Culture*, **1**, 299 (1935).

(10a) It has just come to our attention that G. Blumenfeld, *Ber.*, **74B**, 524 (1941), recently prepared this acid by a different series of reactions. His acid melts at 112° and gave the same *as*-octahydrophenanthrone, m. p. 96°.

ful. The position of the double bond in the α,β-acid (XIV) was proved by its oxidation by means of alkaline permanganate to 2-phenylcyclohexanone.

XII
m. p. 93°

XIII
m. p. 170°

XIV
m. p. 169°

XV
m. p. 114°
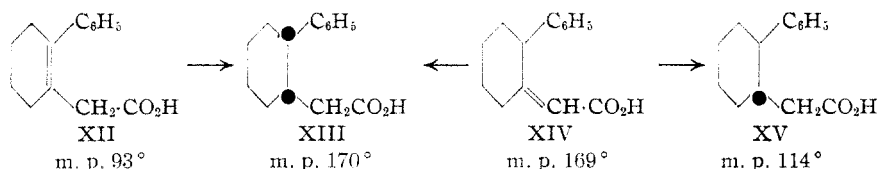
The route through phenylcyclohexylideneacetic acid (XIV) provides the best preparative method for the *trans*-acid (XV) but is still unsatisfactory owing to the difficulty of obtaining the α,β-acid. The yield of the latter from the acetic anhydride dehydration of the corresponding β-hydroxy acid, following Wallach, is low. A somewhat better yield is obtained by the use of *n*-butyric anhydride. If the β,γ-acid is equilibrated with alkali the amount of the α,β-isomer formed is very small. This is to be expected, because not only is cyclohexylideneacetic acid unstable with respect to its β,γ-isomer[11] but the γ-phenyl group further stabilizes the β,γ-form.[12]

Cyclization of the two saturated acids (XIII and XV) by means of sulfuric acid gave the two 9-keto-*as*-octahydrophenanthrenes reported by Cook.[9,12a] Catalytic hydrogenation of each of the two ketones yielded the corresponding pair of secondary alcohols. The *cis*-ketone gave almost completely a 9-hydroxy-*as*-octahydrophenanthrene, m. p. 115–116°, evidently identical with the alcohol described by Cook, Hewett and Lawrence.[9a] An epimeric *cis*-octahydro alcohol, m. p. 133°, was isolated from the products of the perhydrogenation of the *cis*-ketone. On the hypothesis of "catalyst hindrance" discussed in Part I,[13] it seems probable that the more easily prepared epimer has the three hydrogen atoms on the asymmetric carbon atoms, located on the same side of the central ring (XVI). The *trans*-ketone gives two epimeric alcohols, m. p.'s 91° and 101°, the proportion of which appears to vary with the method of hydrogenation. Reduction of the *cis*-ketone by means of sodium and alcohol gave a mixture of secondary

OH
XVI

(11) Linstead, *J. Chem. Soc.*, 355 (1927).
(12) Linstead and Williams, *ibid.*, 2735 (1926).
(12a) The assignment of the *cis*- and *trans*-configuration to these is proved by the evidence reported in the preceding paper (Part V).
(13) Linstead, Doering, Davis, Levine and Whetstone, THIS JOURNAL, **64**, 1985 (1942).

alcohols from which the 116° epimer was isolated. Reduction with aluminum isopropoxide gave an epimeric mixture.

The perhydrogenation of the octahydro-ketones and alcohols was difficult because of the ease with which oxygen was eliminated over the active catalysts required to effect the reaction. This is true in particular of hydrogenation using palladium, and using platinum in acetic acid. The use of platinum in alcohol, however, gave a slow hydrogenation with little elimination of oxygen. In this way *cis*-9-keto-*as*-octahydrophenanthrene yielded a complex mixture from which four products were separated. These melted at 110, 114, 133 and 86°, severally. The first of these was identical with the perhydro-alcohol already obtained by the exhaustive hydrogenation of 9-phenanthrol. It is undoubtedly a *cis-syn-cis*-perhydro-9-phenanthrol and has the configuration represented by IX or X, probably the former. The second product was identical with the *cis-as*-octahydro-9-phenanthrol, m. p. 115–116°, described above (XVI). The product of m. p. 133° was the epimer of this. It has almost the same m. p. as *sym*-octahydro-9-phenanthrol (XI), but is not identical with this substance and depresses its melting point by some 35°. The fourth substance, m. p. 86°, crystallized well but was not homogeneous. Analysis indicated that it was a mixture of perhydro- and octahydro- compounds, and the absorption spectrum also showed the presence of aromatic material. After repeated crystallizations had failed to effect a purification, a method was devised (see experimental part) whereby the substance was separated into the three homogeneous products of the reaction, namely, the perhydro alcohol, m. p. 110° (10%), and the two octahydro-alcohols, m. p. 116° (10%) and m. p. 133° (30%).

Catalytic hydrogenation of the *cis-as*-octahydro-9-phenanthrol, m. p. 116°, over Adams catalyst in alcohol gave mainly the same *cis-syn-cis*-perhydrophenanthrol, m. p. 110°, and a little of the mixture, m. p. 86°.

Very interesting results were obtained from a study of the oxidation of the *cis-syn-cis*-perhydro-alcohol. When this compound was treated with a mixture of chromic and acetic acids at room temperature, it yielded a 9-keto-perhydrophenan-

threne, m. p. 44°. This ketone formed a rather unstable oxime, m. p. 150°. It is undoubtedly *cis-syn-cis*-9-keto-perhydrophenanthrene (I) because on catalytic hydrogenation with platinum in ethyl alcohol it reformed the parent alcohol, m. p. 110°, and on oxidation with nitric acid it yielded *cis-syn-cis*-perhydrodiphenic acid, m. p. 289°. On the other hand, when the same alcohol was oxidized with chromic and acetic acids on the steam-bath a stereoisomeric ketone was obtained. This melted at 57°, depressed the m. p. of the 44° ketone and gave an oxime, m. p. 225°, from which it could be regenerated. Catalytic hydrogenation of the ketone yielded a perhydro-alcohol of m. p. 88–89° and oxidation with nitric acid gave *cis-syn-trans*-perhydrodiphenic acid, m. p. 199°. The new ketone has therefore been formed by inversion of the configuration of one asymmetric carbon atom, and clearly this must be the one adjacent to the carbonyl group. It must therefore have the *trans-syn-cis* configuration (III), and so must the derived alcohol, m. p. 88–89°.

These two ketones are precisely analogous to the α-decalones, studied by Hückel and his collaborators.[14] The *cis-syn-cis* ketone is easily inverted by heat, alkali, and to some extent in the formation of the usual carbonyl derivatives. The fact that the inversion only proceeds at one ring fusion, *i. e.*, to *trans-syn-cis* and not to *trans-syn-trans*, provides clear evidence that it proceeds through an enolization of the carbonyl group from the hydrogen atom on the neighboring bridgehead. The below summarizes the properties of the *cis-syn-cis* ketone in comparison with those of *cis* α-decalone.

	cis-syn-cis-9-Keto-perhydro-phenanthrene	*cis-α*-Decalone[14]
Preparation	Cold CrO₃ on secondary alcohol	Same
Catalytic hydrogenation	Reforms the alcohol without inversion	Same
Nitric acid	Oxidizes without inversion	Same
Vacuum distillation	Unchanged	Same
High temperatures	Inverted at 200°	Inverted at 227°
Oxime	Gives (unstable) *cis-syn-cis*-derivative, m. p. 150°	Gives *trans*-derivative
2,4-Dinitrophenyl-hydrazone	Gives *trans-syn-cis*-derivative, m. p. 236°	...
Alcoholic alkali	Inverted	Inverted

(14) Hückel and Brinkmann, *Ann.*, **441**, 21 (1925); Hückel, Danneel, Gross and Naab, *ibid.*, **502**, 99 (1933).

The formation of *cis-syn-cis*-perhydrodiphenic acid by the nitric acid oxidation of the *cis-syn-cis* ketone (and alcohol) shows the reliability of this method in the determination of configuration. There could have been no reversible enolization and inversion under the experimental conditions and the ketone, in spite of the instability of its configuration, yielded the corresponding acid.

We are now in a position to review the results of Marvel and White[5a] on the hydrogenation of 9-phenanthrol over nickel. They obtained a perhydro-alcohol as a waxy solid, m. p. 67°. This on oxidation with chromic acid, finally on the steam-bath, yielded a ketone of m. p. 57° which was later prepared by another method.[5b] The ketone yielded an oxime, m. p. 219–220°, and a dinitrophenylhydrazone, m. p. 232–233°. On oxidation it gave an acid of m. p. 174°, which Linstead and Doering[2] have shown to be a dimorphous form of *cis-syn-trans*-perhydrodiphenic acid. It is therefore very probable that the ketone of Marvel and White is identical with our *trans-syn-cis* ketone which has the same m. p., and very similar m. p.'s for the derivatives. The configuration of the original hydrogenation product, m. p. 67°, of Marvel and White is, however, uncertain. It may be a *cis-syn-cis*, or a *trans-syn-cis* alcohol, because the conditions of oxidation were such that an inversion was possible. It is obviously not identical with any of our alcohols but there are vacancies for one epimer in each series.

Some preliminary work has been carried out on the perhydrogenation of *trans-as*-octahydrophenanthrene derivatives, but it has not yet reached a stage suitable for report.

The present state of knowledge of the 9-substituted hydrophenanthrenes of known structure is summarized.

Ketones	Alcohols
	sym-Octahydro-9-phenanthrone, m. p. 133° (B.B., L.W.I.)
9-Keto-*as*-octahydrophenanthrenes	*as*-Octahydro-9-phenanthrols
cis liquid (C.H.L., L.W.L.)	m. p. 116° (C.H.L., L.W.L.) / m. p. 133° (L.W.L.)
trans m. p. 96° (C.H.L., L.W.L.)	m. p. 91° (L.W.L.) / m. p. 101° (L.W.L.)
9-Keto-perhydrophenanthrenes	Perhydro-9-phenanthrols
cis-syn-cis m. p. 44° (L.W.L.)	m. p. 111° (L.W.L.) / . . . . .

	Ketones	Alcohols
	9-Keto-perhydrophenanthrenes	Perhydro-9-phenanthrols

trans-syn-cis m. p. 57° (M.W., L.W.L.)

m. p. 89° (L.W.L.)

? m. p. 67° (M.W.)

m. p. 119° (L.W.)

trans-anti-trans m. p. 49° (L.W.)

. . . . .

References: B.B. = von Braun and Bayer[6]
L.W.L. = Linstead, Whetstone and Levine, this paper
C.H.L. = Cook, Hewett and Lawrence[9a]
M.W. = Marvel and White[5a]
L.W. = Linstead and Walpole[1]

An interesting incidental observation was made during attempts to find a better method for the preparation of _trans_-2-phenylcyclohexaneacetic acid. 2-Phenylcyclohexanone was condensed with cyanoacetic ester and the 2-phenylcyclohexylidenecyanoacetic ester (XVII) so formed was reduced, both by aluminum amalgam and catalytically, and subsequently hydrolyzed. The acid isolated in this way was the common (_cis_) 2-phenylcyclohexaneacetic acid, m. p. 169–170° (XIII). The method therefore was of no preparative value as the yield was worse than that obtained by the Reformatsky procedure. The feature of interest was that the initial product of the cyanoacetic ester condensation always deposited a small amount of a crystalline solid on standing and that its analytical values were high both in carbon and hydrogen. It was found that the same solid could be formed by heating the unsaturated cyano ester at 210°. The solid gave figures corresponding to the formula $C_{15}H_{13}ON$, _i. e._, to those required for the unsaturated cyano ester less the elements of ethyl alcohol. It yielded a sodium salt with sodium carbonate, a mono-benzoate and a picrate. It is accordingly assigned the structure 1,2,3,4-tetrahydro-10-cyano-9-phenanthrol (XVIII)

EtOOC—C
|
CN
XVII

ÓH   CN
XVIII
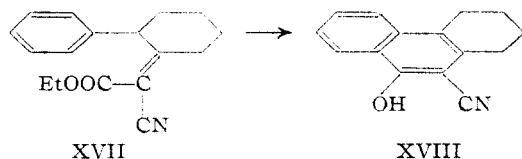
Analogous ring-closures have been observed by McRae and Marion,[15] and by Cope and his collaborators.[16]

(15) McRae and Marion, _Can. J. Research_, **15B**, 480 (1937); Marion and McRae, _ibid._, **18B**, 265 (1940).

(16) Cope, Hofmann. Wyckoff and Hardenbergh, THIS JOURNAL, **63**, 3452 (1941).

Experimental[17]

1. Hydrogenation of 9-Phenanthrol.[18]—9-Phenanthrol was prepared essentially by the method of Fieser, Jacobsen and Price.[19] It was found that very poor yields were obtained unless the sodium (or potassium) acetate was omitted from the reaction mixture. The phenanthrol (9.5 g.) in 200 cc. of glacial acetic acid was hydrogenated in a Parr apparatus using 1.74 g. of Adams catalyst. The theoretical uptake of hydrogen was reached after 188 hours. The product was evaporated to small bulk under reduced pressure in a stream of nitrogen, the residual acid was neutralized and the oil isolated by means of ether. Vacuum distillation separated the product into 4.54 g. of a low fraction (b. p. 120–125° (3 mm.)), 3.22 g. boiling between 150–160° (3 mm.) and 0.54 g. of a residue. Careful fractional distillation of the low fraction yielded a liquid with b. p. 121° (3 mm.), $d^{26.5}_4$ 0.9587, $n^{26.5}$D 1.5088. This material, which is undoubtedly a highly hydrogenated phenanthrene, awaits further investigation.

The high-boiling fractions from the above slowly deposited crystals. Fractional crystallization from hexane yielded _cis-syn-cis_-**perhydro-9-phenanthrol** (IX or X), white needles, m. p. 110.5–111°. The yield of this material from a total of 14.4 g. of 9-phenanthrol was 1.26 g.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.82; H, 11.61.

The alcohol (125 mg.) was added to a mixture of 0.75 cc. of fuming nitric acid and 2.2 cc. of concentrated nitric acid. The mixture was at first warmed gently and then heated on the steam-bath for five minutes. The product was poured into water (15 cc.) and extracted with benzene. The benzene layer was then extracted with sodium carbonate solution. Acidification of the sodium carbonate gave a solid which was purified by a second extraction with sodium carbonate and was then crystallized from acetic acid. The white crystals melted at 278–283° alone, and at 282–285° in admixture with _cis-syn-cis_-perhydrodiphenic acid.

The further investigation of the _cis-syn-cis_-alcohol is described later.

The highest boiling fraction of the original hydrogenation, and the residue, on crystallization from hexane (charcoal) yielded _sym_-**octahydro-9-phenanthrol** (XI). This crystallized from hexane in needles and melted at 134.5–135° (von Braun and Bayer[6] give 133°).

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.22; H, 9.19.

9-Phenanthrol (5 g.) was hydrogenated with 2 cc. of Raney nickel made up to 20 cc. with alcohol, at 120° and an initial pressure of 123 atmospheres. The hydrogen uptake was about 20% above the theoretical for the formation of the octahydro compound. The alcoholic solution of the product turned dull red on exposure to the air. From it there was isolated _sym_-octahydro-9-phenanthrol, m. p. 132–134°, which did not depress the m. p. of the product obtained in the hydrogenation over platinum.

(17) All melting points corrected. Analyses by Miss Eleanor Werble.

(18) The experiments described in the first paragraph were carried out by Mr. D. P. J. Goldsmith, to whom our thanks are due.

(19) Fieser, Jacobsen and Price, THIS JOURNAL, **58**, 2163 (1936).

sym-Octahydrophenanthrene was prepared from tetralin by Schroeter's method,[7] and converted into the sodium salt of the 9-sulfonic acid.[7] The salt was fused with potassium hydroxide at 290–300° in the usual manner. The efficiency of the reaction was greatly reduced by secondary decomposition and the escape of organic vapors (possibly the desired product). At the end, the alkali was dissolved in water neutralized with acid, and the product was extracted with chloroform. The solution was clarified with charcoal, dried and freed from solvent. The residue was crystallized from hexane containing a little activated clay and then deposited sym-octahydro-9-phenanthrol, m. p. 133.5–135°. An attempt to carry out the same fusion in an autoclave failed. The phenol is very difficult to free from colored impurities. It separates from pale solutions in shades ranging from light brown to black. The best method of removing the color is to boil a solution in ligroin (b. p. 90–120°) with activated clay.

2. **2-Phenylcyclohexaneacetic Acids.**—2-Phenylcyclohexanone was condensed with bromoacetic ester following Cook, Hewett and Lawrence.[9a] The hydroxy ester, obtained in 80% yield, was dehydrated by refluxing it (90 g.) for three and a half hours with 60 g. of phosphorus pentoxide and 300 cc. of benzene. A 77% yield of unsaturated ester, b. p. 146–153° (3 mm.), was obtained. This was hydrolyzed with alkali to the β,γ-acid (XII), yield 93%; b. p. 180–190° (3 mm.); m. p. 80–85° (crude); 92–93° after one crystallization from light petroleum (lit., 93°).[9a] The crude unsaturated acid (18 g.) in 75 cc. of glacial acetic acid was hydrogenated with 0.5 g. of palladium catalyst.[20] After eighteen hours at atmospheric pressure, the uptake of hydrogen corresponded to 1.12 mols. The solution was filtered, heated to boiling and diluted with water. The average yield was 63% of the pure cis-2-phenylcyclohexaneacetic acid (XIII), m. p. 168–170° (lit., 169–170°).[9a] The mother liquors from this acid, containing the trans-isomer, were used in the crude state for the preparation of trans-9-keto-as-octahydrophenanthrene.

2-Phenylcyclohexanol-1-acetic ester was hydrolyzed with boiling alkali. The corresponding hydroxy acid, obtained in 75% yield, melted at 128–129°. The acid was converted into 2-phenylcyclohexylidene-acetic acid (XIV) following Cook, Hewett and Robinson.[9b] The yield of the pure α,β-acid, m. p. 168–170°, was only 17%. The by-products of this reaction are still under investigation. When the hydroxy acid was refluxed with n-butyric anhydride for one and one-quarter hours, the α,β-acid was obtained in 35% yield. Both the β,γ- and α,β-acids readily decolorized permanganate in sodium carbonate solution. When the carbonate solutions of the acids were treated with iodine in potassium iodide,[21] the β,γ-acid reacted immediately but the α,β-acid showed no sign of reaction. This difference is in keeping with the structures assigned by Cook.[9] The structure of the α,β-acid was proved by oxidizing 450 mg. of it in sodium carbonate solution with potassium permanganate. The product yielded 220 mg. of 2-phenylcyclohexanone, identified by m. p. and mixed m. p.

The α,β-acid (210 mg.) in 10 cc. of benzene was hydrogenated over 120 mg. of palladium catalyst. In four hours

1.1 mols of hydrogen was taken up. The product was fractionally crystallized from benzene–hexane. It yielded 120 mg. of the cis-acid (XIII), m. p. 158–164°; followed by 70 mg. (33%) of a solid melting at 110–114°. Three crystallizations of the latter from hexane gave trans-2-**phenylcyclohexaneacetic acid** (XV) as thin plates, m. p. 113.5–114.5°.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.33; H, 8.38.

Cyanoacetic Ester Condensations.—Following the general technique of Cope,[22] a mixture of 3.0 g. of 2-phenyl-cyclohexanone, 2.5 g. of cyanoacetic ester, 0.5 g. of ammonium acetate, 0.75 g. of acetic acid and 5 cc. of benzene was heated in a bath at 140–160° for six hours, the benzene being continually replaced. The product was taken up in ether, washed with water and 5% aqueous sodium hydroxide. The solvent was removed and the residue distilled, yield 2.4 g. (52%) of a colorless viscous oil, b. p. 167–174° (3 mm.). The product did not decolorize bromine in carbon tetrachloride but reduced permanganate in acetone. The redistilled product boiled at 174° (4 mm.) and analysis showed that it was mainly **2-phenylcyclo-hexylidenecyanoacetic ester** (XVII).

Anal. Calcd. for $C_{17}H_{19}O_2N$: C, 75.81; H, 7.11. Found: C, 76.46; H, 7.37.

The last drops obtained in the distillation of the above ester solidified to a mass of crystals of **1,2,3,4-tetrahydro-10-cyano-9-phenanthrol** (XVIII), and some of the same solid slowly separated when the original reaction mixture was allowed to stand in the cold. It was also obtained by acidifying the alkaline extracts from the cyano ester. The total yield of the by-product was 8%. It could be prepared by heating the unsaturated cyano ester (XVII) for one and three-quarters hours at 200–220°. It crystallized from benzene in fine white needles, m. p. 230–231°. It was sparingly soluble in alcohol, ether and benzene, and insoluble in sodium bicarbonate solution. With 5% aqueous sodium carbonate it gave an insoluble sodium salt. It gave no color with ferric chloride. Sundry attempts to hydrolyze it failed.

Anal. Calcd. for $C_{15}H_{13}ON$: C, 80.72; H, 5.83; N, 6.28. Found: C, 81.16; H, 5.79; N, 6.19.

The **benzoate**, made by the Schotten-Baumann procedure, crystallized from benzene–hexane in needles, m. p. 183–184°.

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.71; H, 5.24. Found: C, 80.61; H, 5.23.

When warmed with alcoholic picric acid, the cyanophenol yielded a **picrate**, which separated in yellow crystals, m. p. 185–190°, with decomp.

Anal. Calcd. for $C_{21}H_{16}O_8N_4$: C, 55.75; H, 3.56. Found: C, 55.77; H, 3.37.

The picrate regenerated its components when heated with alcohol.

The unsaturated cyano ester (XVII, 1.68 g.) was hydrogenated in alcohol over Adams catalyst, the uptake of hydrogen being 1.03 mols in seven hours. The product was refluxed with 20 cc. of concentrated hydrochloric acid and 5 cc. of water for thirty-six hours. The bulk of the

(20) Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924).

(21) See Bougault, *Ann. chim.*, [8] **14**, 145 (1908); Linstead and May, *J. Chem. Soc.*, 2565 (1927).

(22) Cope and Hoyle, THIS JOURNAL, **63**, 733 (1941).

ester survived hydrolysis; the acid formed melted at 165–168° and was identified as *cis*-2-phenylcyclohexaneacetic acid. Another portion of the unsaturated cyano ester was reduced with aluminum amalgam in moist ether for three days. Hydrolysis as before gave the *cis*-acid, again in poor yield.

3. Derivatives of the *as*-Octahydrophenanthrenes.— *cis*-2-Phenylcyclohexane-1-acetic acid (12.0 g.) was cyclized by means of sulfuric acid following Cook.[9] *cis*-9-Keto-*as*-octahydrophenanthrene (average yield 96%) was obtained as a colorless liquid, b. p. 162–163° (5 mm.).

The ketone (3.5 g.) in 25 cc. of alcohol was treated with 1 mol of hydrogen over Adams catalyst. The product yielded 3.3 g. (93%) of soft, feathery crystals which dried to a chalky mass, m. 112–114°. Two recrystallizations from cyclohexane raised the melting point of the *cis*-**octahydro-9-phenanthrol** to 115–116° (lit., 114–115°).[9] The ultraviolet absorption spectrum was measured in alcohol by Mr. J. J. Leavitt. It had two bands of equal intensity at 266 and 273 mμ with log e_{max}. 2.54.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.10; H, 8.90.

Reduction of the ketone with sodium in alcohol yielded a product melting initially at 60–69°. After a number of crystallizations from cyclohexane this gave some of the same octahydro-alcohol, m. p. 115–116°. Reduction of the ketone with aluminum isopropoxide in isopropyl alcohol gave a solid melting at about room temperature, from which no pure alcohol could be isolated. The ketone (6.0 g.) was hydrogenated over 0.62 g. of palladium catalyst in alcohol, 1.95 mols of hydrogen being taken up in three hours. A small amount (200 mg.) of the 115° alcohol was isolated from the product, but the bulk was a hydrocarbon (4 cc.) which distilled at 121–122° (4–5 mm.) and was presumably *cis-as*-octahydrophenanthrene. The reported boiling point of the latter is 129° (6 mm.).[23]

The isolation of the second epimeric form of the *cis*-alcohol is described below under the perhydrogenations.

trans-9-**Keto-*as*-octahydrophenanthrene.—**The combined mother liquors from the crystallization of *cis*-2-phenylcyclohexylacetic acid were evaporated to a red sirup (25 cc.). This was treated with sulfuric acid as before and the neutral product was crystallized first from light petroleum and then several times from alcohol. The yield of *trans*-ketone was 4.3 g.; m. p. 95–96°, in agreement with Cook, Hewett and Lawrence.[9a] The same ketone was obtained in 74% yield by cyclization of the pure *trans*-acid, m. p. 114°.

The *trans*-ketone (610 mg.) in alcohol, over 120 mg. of Adams catalyst took up 1.0 mole of hydrogen in nineteen hours at atmospheric pressure. Crystallization of the product from hexane and cyclohexane yielded 400 mg. (63%) of a *trans-as*-**octahydro-9-phenanthrol,** sturdy needles melting at 90–91°, and a few milligrams of an *epimer* which formed cotton-like fibers, m. p. 100–101°. A mixture of the two alcohols melted at 84–88°. When a larger preparation was carried out over the same catalyst under a pressure of 3 atmospheres for four days, the proportions of the two alcohols were reversed, the ratio of 101° to 91° form being about 2:1.

(23) Durland and Adkins, This Journal, **60**, 1501 (1938).

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found (m. p. 90–91°): C, 83.29; H, 9.19; (m. p. 100–101°): C, 83.06; H, 9.12.

4. Derivatives of Perhydrophenanthrene.—Hydrogenation of the aromatic ring in the *cis*-octahydro compounds was carried out by means of Adams catalyst in alcoholic solution. The use of acetic acid as a solvent led to elimination of the oxygen atoms. This occurred even when very little acetic acid was present, as is shown by the following experiment. The *cis*-octahydro-9-phenanthrol, m. p. 116°, (2.1 g.) in 15 cc. of acetic acid and 185 cc. of alcohol took up 2.9 mols of hydrogen in five days under an initial pressure of 50 lb. The product was mainly a liquid hydrocarbon but yielded a little solid which on crystallization from hexane gave needles of *cis-syn-cis*-perhydro-9-phenanthrol (100 mg.). This melted at 110–111° alone or in admixture with that prepared from 9-phenanthrol.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.63; H, 11.54.

The hydrocarbon boiled at 109–111° (4 mm.), failed to solidify, and was insoluble in cold concentrated sulfuric acid. Hence it was presumably a perhydrophenanthrene.

cis-9-Keto-*as*-octahydrophenanthrene (10.7 g.) in alcohol was hydrogenated over 0.9 g. of catalyst added in three portions. The uptake of hydrogen was 3.4 mols in eight days. Removal of the solvent and catalyst, followed by crystallization from hexane, yielded 7 g. of solid melting at about 70–85°. On fractional crystallization from cyclohexane, 2.9 g. of the *cis*-octahydro alcohol, m. p. 112–114°, was obtained. The residue was crystallized from ether, which yielded 2.4 g. of the *cis-syn-cis*-perhydro alcohol, m. p. 108–110°. These substances were identified by mixed m. p. determinations. The ethereal mother liquors deposited 0.2 g. of the epimeric *cis-as*-**octahydro-9-phenanthrol,** m. p. 126–128°, which after repeated crystallization from hexane gave fine needles, m. p. 132.5–133.5°. A mixture of this with the *cis-as*-octahydro alcohol (m. p. 115–116°) melted at 95–100°. A mixture with *sym*-octahydro-9-phenanthrol (m. p. 133°) melted at 95–105°. The new *cis-as*-octahydro alcohol differs from the isomeric *sym*-octahydro phenol of the same m. p. in that it is readily obtained and kept in a pure white crystalline form. The *sym*-octahydro phenol discolors very readily, as already noted.

Anal. Calcd. for $C_{14}H_{18}O$ (alcohol, m. p. 132.5–133.5°): C, 83.12; H, 8.97. Found: C, 82.94; H, 8.82.

The mother liquor from the original 7 g. of solid slowly deposited a further 1.4 g. of solid, which crystallized in rosets of thick spikes, m. p. 85–87°. Repeated crystallization from alcohol, ether and hydrocarbon solvents failed to alter this. This substance, however, gave analytical figures (C, 81.08; H, 10.41) intermediate between those required for an octahydro and a perhydro alcohol. The ultraviolet absorption spectrum (for which we are indebted to Mr. J. J. Leavitt) showed the two equal bands, with maxima at 266 and 273 mμ which are present in the spectrum of *cis-as*-octahydro-9-phenanthrol. The intensity (log e_{max}. 2.2) corresponded to the presence of about 50% of this compound. The solid, m. p. 85–87°, was dissolved in acetic acid and the solution diluted with small portions of water. Crude *cis-syn-cis* perhydro alcohol

(10% of solid) then separated, and, after crystallization from ether, melted at 108–110°. Further dilution of the acetic acid gave the common *cis-as*-octahydro alcohol (10%), which melted at 115–116° after crystallization from cyclohexane. Removal of the acetic acid left an oil which was hydrolyzed with cold 10% alcoholic potash for forty-eight hours. Acidification and crystallization of the solid product yielded the epimeric *cis-as*-octahydro alcohol, m. p. 133°, (30%). The three components were identified by mixed m. p. determinations.

The *cis-as*-octahydro-9-phenanthrol of m. p. 112–114° was hydrogenated over platinum in alcohol in the same way. It yielded 47% of *cis-syn-cis*-perhydro-9-phenanthrol, m. p. 108–110°, and 10% of the mixture of m. p. 85–87°.

cis-syn-cis-**9-Keto-perhydrophenanthrene.**—Chromic acid (1.0 g.), dissolved in 5 cc. of 80% acetic acid, was added to an ice-cooled solution of 2.3 g. of *cis-syn-cis*-perhydro-9-phenanthrol, m. p. 110–111°, in 30 cc. of glacial acetic acid. The mixture was left overnight at room temperature, poured into water and extracted with ether. The ether was washed with water and sodium carbonate solution. Evaporation of the dried ether solution *in vacuo* left 2.0 g. (87%) of an oil which crystallized to a solid, m. p. 35–38°. The material could be distilled unchanged at about 130° (3 mm.). Six crystallizations from cold petroleum ether gave short needles of the *cis-syn-cis*-perhydro ketone, m. p. 43–44°.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.69; H, 10.42.

The **oxime** was obtained by leaving the ketone in cold aqueous alcoholic solution with hydroxylamine hydrochloride and sodium acetate for four hours. The crystals so obtained melted at 150–151° and were rendered less pure by crystallization, presumably owing to the occurrence of inversion. For analysis the first precipitated crystals were washed with water and petroleum ether and dried.

Anal. Calcd. for $C_{14}H_{23}ON$: C, 75.97; H, 10.47. Found: C, 76.24; H, 10.28.

Recrystallization from hot alcohol lowered the m. p. to 143–146°. When an alcoholic solution was boiled for three hours, the crystals which separated melted at 135–141°.

The **2,4-dinitrophenylhydrazone** formed orange plates from hot alcohol, m. p. 236–238°, decomp. The **semicarbazone** melted at 195–205° without crystallization, at 205–220° after one crystallization from hot alcohol, and at 210–218° after four hours of boiling with alcohol.

The ketone (200 mg.) was heated for fifteen minutes on the steam-bath with 3 cc. of a mixture of 5 cc. concentrated and 3 cc. fuming nitric acid. The product was poured on ice, the yellow resin taken up in ether. The ethereal solution was extracted four times with saturated aqueous sodium bicarbonate. The extract was acidified, the acid isolated by means of ether, boiled with charcoal in acetone and crystallized from benzene. *cis-syn-cis*-Perhydrodiphenic acid (10 mg.) separated, m. p. 275–280°, mixed m. p. 279–284°. The identity was confirmed by converting the acid (3 mg.) into the dimethyl ester, which melted at 66–69° alone and at 71–73° in admixture with authentic material.

Catalytic hydrogenation of the ketone over Adams cata-

lyst in alcohol yielded the *cis-syn-cis*-perhydro-9-phenanthrol of m. p. 110°.

trans-syn-cis-**9-Keto-perhydrophenanthrene.**—*cis-syn-cis*-Perhydro-9-phenanthrol, m. p. 110°, was oxidized with chromic and acetic acids in the manner described above with the difference that after the initial reaction, the mixture was heated on the steam-bath for fifteen minutes. The *trans-syn-cis*-ketone, isolated in the same way as its isomer, crystallized from petroleum ether in needles, m. p. 56.5–57.5°. A mixture of the two ketones was liquid at room temperature.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.65; H, 10.80.

The same perhydro alcohol (1.9 g.) was oxidized following Oppenauer's method by refluxing it for eight hours with 1.4 g. of aluminum *t*-butoxide in a mixture of acetone and benzene. The product was a mixture of the two ketones melting at about 25° and not easily separable by crystallization. It was accordingly heated in an atmosphere of nitrogen at 200° for one and three-quarters hours. The product was the nearly homogeneous *trans-syn-cis* ketone, m. p. 48–52°, identified by a mixed m. p. determination. The same inversion was achieved by refluxing the mixed ketone, m. p. 25°, with alcoholic sodium ethoxide for one and one-half hours.

The **oxime** of the *trans-syn-cis* ketone formed immediately at room temperature and crystallized in fine needles, m. p. 224–225°. A mixture with the *cis-syn-cis* oxime (m. p. 150–151°) melted over the range 143–180°.

Anal. Calcd. for $C_{14}H_{23}ON$: C, 75.97; H, 10.47. Found: C, 76.25; H, 10.38.

When the oxime was boiled for six hours with 5% sulfuric acid, it regenerated the *trans-syn-cis* ketone, m. p. 57°.

The **2,4-dinitrophenylhydrazone** formed red plates from hot alcohol, m. p. 236–237°, decomp. The color was more intense than that of the corresponding derivative made from the *cis-syn-cis* ketone but the mixed m. p. was the same (236–237° decomp.) and it is probable that both ketones give the same derivative.

The ketone (200 mg.) was oxidized with nitric acid as described for the *cis-syn-cis*-isomer. The product yielded 30 mg. of *cis-syn-trans*-perhydrodiphenic acid, m. p. 196–198° alone, and 197–198° in admixture with an authentic sample (m. p. 198–199°). Hydrogenation of the ketone (130 mg.) over Adams catalyst in alcohol led to a theoretical uptake of hydrogen. The *trans-syn-cis*-**perhydro-9-phenanthrol** so obtained was crystallized first from hexane and then from ether, from which it separated in rosets of long prisms, m. p. 88–89°.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.19, 80.21; H, 11.38, 11.33.

Summary

Catalytic hydrogenation of 9-phenanthrol over platinum yields *cis-syn-cis*-perhydro-9-phenanthrol, m. p. 111°, together with a small amount of *sym*-octahydro-9-phenanthrol. The latter substance was also obtained over nickel at 120°. Its structure was proved by its synthesis from *sym*-octahydrophenanthrene.

cis-9-Keto-as-octahydrophenanthrene yields two secondary alcohols, m. ps. 116° and 133°. The isomeric trans-ketone also yields two epimeric alcohols, m. ps. 91° and 101°.

Hydrogenation of cis-9-keto-as-octahydrophenanthrene over platinum in alcohol gives cis-syn-cis-perhydro-9-phenanthrol and the two octahydro alcohols. Hydrogenation of cis-as-octahydro-9-phenanthrol gave the same cis-syn-cis-perhydro alcohol. When the cis-syn-cis-perhydro alcohol was oxidized by chromic acid at 0–25° it yielded cis-syn-cis-9-keto-perhydrophenanthrene. However, when the same oxidation was completed at 100° the product was the isomeric ketone with the trans-syn-cis configuration, presumably identical with a ketone isolated by Marvel and co-workers. The inversion of the cis-syn-cis ketone

has been studied and is correlated with that of cis-α-decalone.

The cis-syn-cis-perhydro alcohol and ketone were oxidized by nitric acid to cis-syn-cis-perhydrodiphenic acid. The trans-syn-cis ketone yielded cis-syn-trans-perhydrodiphenic acid on nitric acid oxidation and a new perhydro alcohol on catalytic hydrogenation.

Three forms of the perhydrophenanthrene ring have therefore been made and oriented.

Pure trans-2-phenylcyclohexaneacetic acid has been obtained, m. p. 114°. When heated to 200°, 2-phenylcyclohexylidenecyanoacetic ester spontaneously cyclizes to tetrahydro-10-cyano-9-phenanthrol.
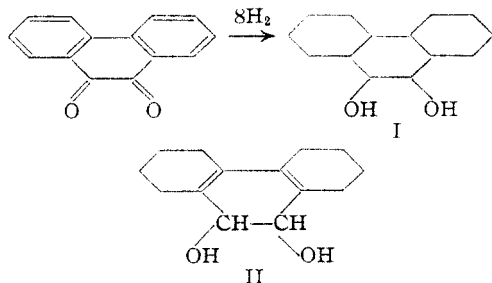
CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 30, 1942

The Stereochemistry of Catalytic Hydrogenation. VII. The Complete Hydrogenation of Phenanthraquinone

BY R. P. LINSTEAD AND PHILIP LEVINE

The catalytic hydrogenation of 9,10-phenanthraquinone has already been investigated by von Braun and Bayer[1] and by Skita,[2] but they did not succeed in bringing about the complete hydrogenation of the molecule. Skita observed a reduc-

tion over colloidal platinum to sym-decahydro-9,-10-dihydroxyphenanthrene (II). von Braun and Bayer, working with a nickel catalyst at high temperatures, also observed a preferential hydrogenation of the lateral rings, but their products suffered a partial or complete removal of the oxygen atoms.

We find that phenanthraquinone can be completely hydrogenated both over platinum at room temperature and over Raney nickel at 160° without loss of oxygen. Eight molecular proportions

of hydrogen are taken up and the products are perhydro-9,10-dihydroxyphenanthrenes (I). Four beautifully crystalline stereoisomers of this structure have been obtained.

When the hydrogenation was carried out under about 4 atmospheres pressure over Adams platinum oxide in acetic acid solution, a homogeneous glycol, m. p. 174°, was obtained. Over Raney nickel in ethanol at 160° and about 170 atmospheres the reaction yielded principally two isomeric glycols, melting at 174 and 155°, respectively, together with a very small amount of a fourth isomer of m. p. 184°. The glycol of m. p. 174° obtained over nickel differed in crystalline form from that of the same m. p. obtained by the use of platinum, depressed its melting point, and gave a different dibenzoate. All the four products gave analyses corresponding to the perhydroglycol structure, $C_{14}H_{24}O_2$, and yielded distinct dibenzoates. They gave positive Criegee tests for 1,2-glycols.[3]

Corresponding to the six inactive stereoisomeric forms of the fundamental perhydrophenanthrene skeleton[4] there are twenty inactive 9,10-glycols. Each of the cis-cis and trans-trans

(1) von Braun and Bayer, Ber., 58, 2667 (1925).

(2) Skita, ibid., 58, 2685 (1925).

(3) Criegee, ibid., 64, 260 (1931).

(4) Linstead and Walpole, J. Chem. Soc., 842 (1939); Linstead, Whetstone and Levine, THIS JOURNAL, 64, 2014 (1942).