

Mono-nitro Derivative.—The *trans*-acid (96 mg.) was nitrated in the same manner as the *cis*- (*vide supra*) to obtain 116 mg. of the crude product, m. p. 212–217°. Two recrystallizations from acetone–benzene gave 65 mg. of irregular prisms, m. p. 218–219°. Further recrystallization from water, under such conditions that the substance separated as an oil and subsequently crystallized, gave material of similar appearance and m. p. Crystallization of 40 mg. from water, with slow cooling, gave 32 mg. of needles, m. p. 224–225°. The mixed m. p. with the low-melting material was 224–225°. The mixed m. p.'s of both forms with either form of the nitro derivative from the *cis*-acid showed depressions to about 185°.

Anal. Calcd. for $C_{14}H_{10}O_2N$: C, 57.34; H, 5.16. Found: C, 57.43; H, 5.12.

Hydrogenation.—The *trans*-acid (2 g.) in 200 cc. of acetic acid was hydrogenated over 550 mg. of Adams catalyst. The theoretical uptake of hydrogen (3 moles) occurred in one hundred minutes, after which there was no appreciable reaction. No precipitate separated. The catalyst was filtered and the solvent removed. The granular residue was crystallized from acetic acid, a seed of *cis-syn-trans*-perhydrodiphenic acid being introduced. The first crop, 1.60 g. (78%), melted at 190–194° alone, at 192–197° in admixture with *cis-syn-trans*-perhydrodiphenic acid (m. p. 198–200°) and at 192–196° after a further crystallization. As the m. p. of the *cis-syn-trans* acid is sensitive to traces of impurities, this material may be taken to be the nearly pure isomer. The mother liquor from this acid was submitted to an exhaustive fractional crystallization. It yielded three products: (a) more of the *cis-syn-trans* perhydro acid, bringing the total yield up to 84%; (b) about 10 mg. of an unsaturated acid, m. p. 210–211.5°, identical with material already isolated by Mr. Doering; (c) about 3 mg. of what was apparently another unsaturated acid. This formed soft needles of m. p. 261–264°, depressed the m. p. of the *cis-syn-cis* perhydro acid and readily reduced 0.5% potassium permanganate in aqueous

sodium bicarbonate solution. (Under the same conditions the hexahydro- and perhydrodiphenic acids require from eight to twenty-four hours for a discharge of the color of one drop of 0.5% permanganate.) During this fractional crystallization, the solution was frequently seeded with *cis-anti-trans* perhydrodiphenic acid (m. p. 206°), but none of this substance separated, and it can safely be concluded that it is either wholly or almost completely absent.

The pure *trans*-anhydride (150 mg.) was heated for one hour at 243 ± 3°. A little carbon dioxide was evolved, indicating the formation of some pyroketone. The acidic portion of the product was isolated by means of alkali and was crystallized from acetic acid. Seeding with the *cis*-hexahydro acid yielded three crops of this material (total, 20 mg.) and further seeding gave no more of it. The solution was accordingly seeded with the *trans*-hexahydro acid, which yielded five crops of *trans*-acid, totalling 45 mg. The acids were identified by m. p. and mixed m. p.

Summary

Half-hydrogenation of diphenic acid over platinum yields *cis*-hexahydrodiphenic acid. Thermal inversion of this acid yields the *trans*-isomer. Both the acids and their anhydrides yield mixtures rich in the *trans*-isomer when heated. The two acids yield distinct mono-nitro derivatives.

Further catalytic hydrogenation of the *cis*-hexahydro acid yields *cis-syn-cis*-perhydrodiphenic acid, and hydrogenation of the *trans*-hexahydro acid yields *cis-syn-trans*-perhydrodiphenic acid. The integrity of the configuration already established is therefore preserved, and further hydrogenation goes *cis*- and *syn*-.

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The Stereochemistry of Catalytic Hydrogenation. V. The Assignment of *cis*- and *trans*-Configurations

BY R. P. LINSTEAD, SELBY B. DAVIS AND RICHARD R. WHETSTONE

The stereochemical problem connected with the perhydrodiphenic acids which is left unsolved in the preceding papers is the allocation of *cis*- and *trans*-configurations to the terminal acids.¹ It has been shown that the 289 and 223° acids between them constitute the *cis-syn-cis* and *trans-syn-trans* acids, and the 198 and 247° acids share the *cis-anti-cis* and *trans-anti-trans*-configurations. There are many indications that the 289° and the 198° acids are the *cis*-members of the two series.

(1) Linstead and Doering, *THIS JOURNAL*, **64**, 2003 (1942).

The work described in the present paper proves this to be true.

The 289° perhydro acid has two similar arrangements of the carboxyl groups with respect to the backbone. It is made by the hydrogenation of the hexahydro acid of m. p. 242° by a method not involving an inversion.² Hence the configuration of the 242° acid is repeated twice in the 289° acid.

We therefore examined the configuration of

(2) Linstead and Davis, *ibid.*, **64**, 2006 (1942).

this hexahydro acid by oxidizing away the aromatic ring and leaving a cyclohexane derivative of known configuration. Treatment of the acid with a mixture of concentrated and fuming nitric acids gave only nitration in the aromatic ring and permanganate oxidation also yielded no useful products. Ozonization, however, gave the desired information.

The acid was treated in acetic acid solution with ozonized oxygen and subsequently with hydrogen peroxide. The acidic product was separated by means of the fractional acidification technique which has already been described.³ This effected a simple separation of the starting material and another acid which after one crystallization melted at 185–188° and was nearly pure *cis*-hexahydrophthalic acid (I). It was identified by direct comparison of the free acid with authentic material and by conversion into the known *cis*-dianilide, m. p. 238°. ^{4b} The *cis*-configuration of the latter was confirmed by the fact that it readily yielded the phenylimide (II) when boiled with acetic acid. The dianilide of *trans*-hexahydrophthalic acid, which was separately made for comparison, melted at 317–318° and failed to yield a phenylimide under the same conditions.

The *cis*-configuration of this form of hexahydrophthalic acid is known with certainty.⁴ In the present work *cis*-hexahydrophthalic acid was formed in a yield of 44% by a mild series of operations in which there is no possibility of an inversion. Moreover, it must be borne in mind that the *cis*- is the *unstable* configuration and that any inversion would tend to yield a *trans*-product.

This evidence conclusively proves that the acid of m. p. 242° is *cis*-hexahydrodiphenic acid (III). Hence the acid of m. p. 289° is *cis-syn-cis*-perhydrodiphenic acid (IV) and the double invert acid, m. p. 223°, has the *trans-syn-trans*-configuration. It follows that among the diphenic acids, catalytic hydrogenation over platinum yields *cis*-products which can be inverted by chemical means into the *trans*-isomers. The usual rule-of-thumb generalizations are therefore correct in this series.

It is shown in the following paper⁵ that the 289° acid is related to a 9-ketoperhydrophenanthrene of m. p. 44° (V). This ketone is easily

inverted by the action of heat or bases into an isomer of m. p. 57°, which yields *cis-syn-trans*-perhydrodiphenic acid on oxidation. There is a complete analogy with Hückel's related experiments with dicyclic compounds and the rearrangement of the ketone corresponds precisely with the conversion of *cis*- α -decalone to its *trans*-isomer.

The chemical inversions of the *syn*-keto-hydrophenanthrenes and of the *syn*-hydrodiphenic acids accordingly fall into line with those of related substances of simpler structure. We may therefore make the corresponding deductions in the *anti*-series with confidence, thus: (1) Among the *anti* compounds the perhydro acid of m. p. 198° is the direct hydrogenation product and yields the isomer of m. p. 247° by double inversion. Hence these substances are *cis-anti-cis* (VIII) and *trans-anti-trans* (IX), respectively.

(2) The 247° acid has been prepared⁶ by the oxidation of a 9-keto-perhydrophenanthrene of m. p. 49° which was stable to heat and alkali.⁷ Hence the ketone will have a *trans*-fusion of the rings next to the keto group. Hence the 247° acid contains at least one *trans*-carboxyl; but as it is a terminal acid, it must have two such arrangements and be the *trans-anti-trans*-isomer. The 49° ketone must have the same configuration (X) and this is supported by the physical properties of the related perhydrophenanthrene.⁷

We have obtained independent evidence supporting these configurations from the following experiments. The 49° ketone is made by the catalytic hydrogenation of an olefinic ketone, m. p. 89°, originally prepared by Rapson and Robinson.⁸ (The method of preparation of the unsaturated ketone itself supports a *trans*-configuration for its one-ring fusion.) We find that ozonization of the unsaturated ketone gives a δ -keto acid, C₁₃H₂₀O₃, isolated as a crystalline oxime. This is assigned the formula XII. Its formation shows the correctness of the Δ^{10} -9-keto-dodecahydrophenanthrene structure (XI) assigned to the unsaturated ketone by Rapson and Robinson. On acetylation and subsequent pyrolysis by the general method of Thiele⁹ the keto acid was converted into an unsaturated lactone. This was not obtained as a homogeneous substance but contained some of the isomer (XIII) with the double bond adjacent to the backbone.

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

(4) (a) Werner and Conrad, *Ber.*, **32**, 3046 (1899); (b) Stoermer and Steinbeck, *ibid.*, **65**, 413 (1932).

(5) Linstead, Whetstone and Levine, *THIS JOURNAL*, **64**, 2014 (1942).

(6) Linstead and Walpole, *J. Chem. Soc.*, 850 (1939).

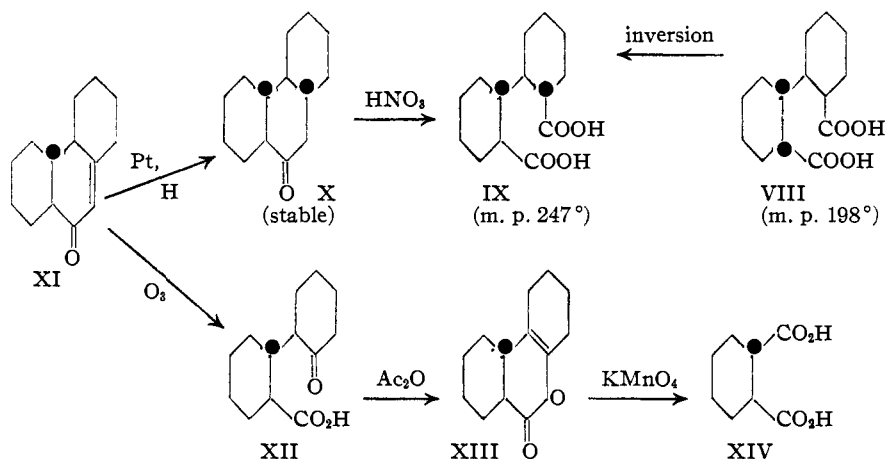
(7) Linstead and Walpole, *ibid.*, 842 (1939).

(8) Rapson and Robinson, *ibid.*, 1285 (1935).

(9) Thiele, Tischbein and Lossow, *Ann.*, **319**, 180 (1901).

On oxidation with permanganate the lactone gave *trans*-hexahydrophthalic acid (XIV), in poor yield. Hence all the substances mentioned above have a *trans*-configuration. Some of the reactions used in this degradation were comparatively vigorous and the final product has the stable configuration. Hence, we do not regard this evidence as so unequivocal as that given above for the oxidation of *cis*-hexahydrodiphenic acid.

The most important configurational evidence in the *anti*-series is summarized in the following scheme

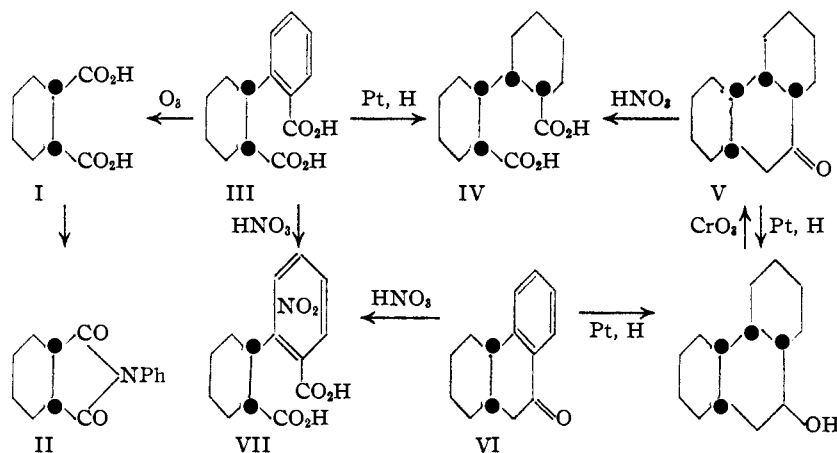


Finally, we have been able to establish two other stereochemical connections between the

threne (VI). When the octahydro ketone was treated with nitric acid it yielded the mono-nitro derivative of *cis*-hexahydrodiphenic acid (VII). Hence it must have the *cis*-configuration. Its *trans*-isomer has been similarly oxidized and nitrated to the nitro-derivative of *trans*-hexahydrodiphenic acid. (A number of nitro-ketones are obtained as by-products in these oxidations. They are described in the experimental section.)

The stereochemical relationships between the tricyclic and dicyclic compounds are therefore firmly established by a number of independent

links. The more important connections in the *syn*-series are indicated in the scheme



tricyclic compounds and the hydrodiphenic acids. It has already been pointed out that the 289 and 200° acids are related to the 44 and 57° perhydro ketones, respectively. In the next paper it is shown that the 44° ketone can be formed (through the corresponding perhydro alcohol) by the hydrogenation of a 9-keto-*as*-octahydrophenan-

Experimental¹⁰

Ozonization of *cis*-Hexahydrodiphenic Acid.—The acid, m. p. 240–241°,² (1.00 g.) was dissolved in 20 cc. of warm glacial acetic acid and ozonized for four hours. The product was allowed to stand overnight with 50 cc. of 3% hydrogen peroxide and evaporated almost to dryness on the

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

steam-bath in a current of air. The residue was then heated on the steam-bath for two hours with a further 25 cc. of 3% hydrogen peroxide and evaporated to dryness. The mainly crystalline residue was dissolved in 15 cc. of 10% aqueous sodium carbonate, a trace of insoluble material filtered off and the solution washed with ether. The alkaline solution was heated to boiling and concentrated hydrochloric acid added in drops to incipient crystallization. The subsequent fractional acidification by the method described in earlier papers^{2,3} gave the following results

Fraction	Approx. vol. of concd. HCl, cc.	Weight, mg.	M. p., °C.	Identity
1	2.5	260	234-237	} <i>cis</i> -Hexahydrodiphenic acid
2	0.5	240	237-239	
3	0.5	Trace of tar
4	0.5	9.1	174-181	} <i>cis</i> -Hexahydrophthalic acid
5	1.0	82.2	177-184	
6	1.0	36.5	181-186	

A further 0.5 cc. of hydrochloric acid was added to the final mother liquor and the solution extracted with ether to give 0.11 g. of semi-crystalline residue.

Fractions 1 and 2 were identified as unchanged starting material by mixed m. p. Fractions 4, 5 and 6 in admixture with authentic *cis*-hexahydrophthalic acid (m. p. 191.5-192.5°) melted at about 185°. After one recrystallization from 80% acetic acid, nearly pure *cis*-hexahydrophthalic acid was obtained, m. p. 185-188°, mixed m. p. 186-189°. Recrystallization of the residue from the ether extract yielded 23 mg. of additional *cis*-hexahydrophthalic acid, m. p. 183-188°, mixed m. p. 185-189°.

The crystallized acid (53 mg.) was converted into the acid chloride by means of phosphorus pentachloride (130 mg.) in dry ether (3 cc.). After twenty minutes the solvent was removed and the residue evacuated at the water pump for half an hour. The residue was dissolved in 2 cc. of ether and treated with 120 mg. (2 mols) of aniline in 2 cc. of ether. The mixture was freed from solvent, the residue taken up in the minimum quantity of 95% alcohol (ca. 4 cc.), the solution filtered and allowed to cool. The dianilide of *cis*-hexahydrophthalic acid (43 mg.), so obtained, melted at 227-229° and after one crystallization from alcohol formed colorless needles, m. p. 237.5-238°.

Anal. Calcd. for C₂₀H₂₂O₂N₂: C, 74.50; H, 6.88. Found: C, 74.75; H, 6.70.

The dianilide was further identified by refluxing it for eighteen hours with 80% acetic acid which yielded the phenylimide (II), flat prisms from methanol, m. p. 131-132°. The m. p.'s of the dianilide and phenylimide prepared from authentic *cis*-hexahydrophthalic acid were the same and were not depressed by admixture with the above samples. For these substances Stoermer and Steinbeck^{4b} give m. p.'s 234° (dianilide) and 132° (phenylimide).

Attempted oxidation of *cis*-hexahydrodiphenic acid with a mixture of fuming and concentrated nitric acids gave an acidic product, from which the only homogeneous substance which could be isolated was nitro-*cis*-hexahydrodiphenic acid, m. p. 219-220°. This was identical with the material described in Part IV.² Treatment of *cis*-hexahydrodiphenic acid with alkaline permanganate at

60-80°, left it largely unchanged and no useful products were isolated.

Oxidation of *trans*- Δ^{10} -9-Keto-dodecahydrophenanthrene (XI).—The unsaturated ketone was prepared from acetylcyclohexene by the method of Rapson and Robinson.⁸ Preliminary experiments on the oxidation with nitric acid, permanganate, hypobromite and ozone indicated that the last-named reagent was the most suitable.

The ketone (8.9 g.) dissolved in 15 cc. of glacial acetic acid was treated with a current of ozonized oxygen for three hours. The product was refluxed for forty minutes with 45 cc. of water and 0.5 cc. of concentrated hydrochloric acid and then separated into neutral and acid fractions. The neutral fraction yielded 5.36 g. which was again ozonized and the product separated as before. The combined acid product from the two ozonizations was treated with 50 cc. of alcohol, 50 cc. of 10% aqueous sodium hydroxide and 4.6 g. of hydroxylamine hydrochloride. The mixture was refluxed for two hours, cooled, acidified with acetic acid and left overnight at 5°. An oxime separated, 3.07 g., m. p. 160-161°. Evaporation of the filtrate yielded material which separated as an oil and subsequently solidified in brown lumps, m. p. ca. 100-130°, 3.15 g. Crystallization of the first fraction from alcohol gave the pure oxime of *trans*-2-keto-1,1'-dicyclohexyl-2'-carboxylic acid (XII), m. p. 162-163°.

Anal. Calcd. for C₁₃H₂₁O₃N: C, 65.24; H, 8.85. Found: C, 65.64, 65.61; H, 8.92, 8.99.

When the oxime (3.07 g.) was refluxed with 10% hydrochloric acid (100 cc.) for two hours it regenerated the keto-acid as a pale yellow liquid which failed to solidify (yield: 2.45 g.). The keto-acid (1.31 g.) was refluxed for five hours with acetic anhydride (6 cc.), and the excess of reagent was then removed at about 65°, under reduced pressure. The residue was dissolved in ether, freed from acids by means of sodium bicarbonate solution, and isolated by removal of the ether, 1.12 g. of an orange oil being obtained. This lactone (partly XIII) was insoluble in aqueous sodium hydroxide in the cold but dissolved slowly on warming. Dissolved in acetone it decolorized alkaline permanganate. The equivalent was determined by warming the lactone for an hour with an excess of 0.1 *N* alkali and back-titration. *Anal.* Calcd. for C₁₃H₁₈O₃: equiv., 206.3. Found: equiv., 203.

The unsaturated lactone (1.1 g.) was suspended in a mixture of 100 cc. of acetone and 50 cc. of 5% sodium bicarbonate solution. To the solution, mechanically stirred at 0°, 100 cc. of 0.5% potassium permanganate solution was added during one-half hour, followed by 100 cc. of 1% permanganate solution during one hour and, finally, 60 cc. of 3% permanganate solution during one hour. Reduction of the permanganate was slow after the addition of the 1% solution. The mixture was finally allowed to come to room temperature and, after standing for two hours, was freed from manganese dioxide by filtration, and the filtrate and washings evaporated nearly to dryness. This residual solution was filtered, acidified with acetic acid and freed from carbon dioxide by boiling. A solution of barium acetate was then added which precipitated a mixture of barium salts, including that of *trans*-hexahydrophthalic acid. After various attempts by other methods

this acid was isolated as follows. The free acids were obtained as a glassy solid (1.02 g.) by treatment of the precipitate and filtrate with hydrochloric acid and extraction with ether. The glassy solid (0.70 g.) was dissolved in 10 ml. of boiling 10% sodium carbonate solution and the insoluble portion discarded. The solution was then fractionally acidified by the standard procedure. The early fractions were glassy solids, but the final fraction consisted of 9 mg. of a light brown, microcrystalline powder melting at 203–213° in the crude state and 216–223° after crystallization from water. The mixed m. p. of the crude material with authentic *trans*-hexahydrophthalic acid (m. p. 227–229°) was 212–217°, but the m. p. of *cis*-hexahydrophthalic acid was considerably depressed. The identity was confirmed by conversion to the anhydride with acetyl chloride, m. p. and mixed m. p. 142–144°. Extraction of the mother liquor from the fractional precipitation with ether gave a semi-crystalline residue from which 21 mg. of additional *trans*-hexahydrophthalic acid, m. p. 219–223°, was obtained by crystallization from aqueous acetic acid. This was treated with phosphorus pentachloride and aniline, as previously described for the preparation of the *cis*-compound, and the product crystallized from glacial acetic acid to give 10 mg. of the dianilide, colorless needles, m. p. (block preheated to 260°) 317–318°. The mixed m. p. with the dianilide of similar m. p. prepared from authentic *trans*-hexahydrophthalic acid showed no depression.

Anal. Calcd. for $C_{20}H_{22}O_2N_2$: C, 74.50; H, 6.88. Found: C, 74.27; H, 6.78.

It may be observed in passing that the m. p.'s of *trans*-hexahydrophthalic acid given in the literature are in the range 215–220° (see *e. g.*, reference 4). We find that by repeated crystallization from water it is possible to isolate the acid as prisms, m. p. 227–229°. The m. p. of the impure acid is considerably affected by the rate of heating, that of the pure acid less so. The above m. p. was obtained by introducing the acid into a bath at 200°. The pure acid of m. p. 227–229° yields the anhydride with the m. p. (142.5–144°) recorded in the literature.

Action of Nitric Acid on *cis*- and *trans*-9-Keto-*as*-octahydrophenanthrenes.—The two stereoisomeric 9-keto-*as*-octahydrophenanthrenes were prepared essentially by the methods of Cook and his co-workers¹¹ as described in the following paper.⁵ The liquid ketone (*cis*-) (0.4 g.) was heated on the steam-bath for fifteen minutes with 5 cc. of concentrated nitric acid and 3 cc. of fuming nitric acid. The product was poured on ice and separated into neutral and acidic fractions by means of sodium carbonate solution. Acidification of the sodium carbonate solution yielded 20 mg. of *cis*-nitro-hexahydrodiphenic acid (VII) as a yellow solid, which was isolated by means of ether. It melted at 200–208° in the crude state, at 208–210° after one crystallization from acetone–benzene and at 217–219° in admixture with an authentic sample of the high-melting form (m. p. 218–219°) prepared as described in the preceding paper.² The neutral fraction from this reaction yielded 0.1 g. of a crystalline **trinitro-ketone**, which formed clear plates, m. p. 151.5–152° from hexane.

Anal. Calcd. for $C_{14}H_{13}N_3O_7$: C, 50.15; H, 3.91. Found: C, 50.57; H, 4.18.

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

This substance agrees in m. p. but not in analysis with the mononitro ketone reported by Cook, *et al.*¹¹ When the *cis*-octahydro ketone (500 mg.) was heated for thirty minutes on the steam-bath with 1 cc. of concentrated and 1 cc. of fuming nitric acid in 10 cc. of acetic acid, it gave 300 mg. of a neutral solid. After recrystallization from acetic acid and then from benzene–hexane, this formed colorless plates, m. p. 95–96.5°, and analysis showed it to be a **dinitro-ketone**. Its m. p. was depressed by admixture with the nitro-ketone of m. p. 152°.

Anal. Calcd. for $C_{14}H_{13}N_2O_5$: C, 57.93; H, 4.86. Found: C, 57.87; H, 4.55.

Further treatment of the dinitro-ketone with nitric acid on the steam-bath yielded the trinitro-ketone of m. p. 152°.

The dinitro-ketone very probably contains the nitro-groups ortho- and para- to the backbone. The introduction of a third nitro-group is abnormal and it is probable that it corresponds with an attack on the alicyclic portion of the molecule.

Oxidation of *cis*-9-keto-*as*-octahydrophenanthrene with hot chromic acid in acetic acid, or with alkaline permanganate, gave no useful products.

trans-9-Keto-*as*-octahydrophenanthrene (350 mg., m. p. 95°) was heated for fifteen minutes with 4 cc. of concentrated and 4 cc. of fuming nitric acid. The product was separated as before. Crystallization of the acid fraction from acetic acid yielded *trans*-nitro-hexahydrodiphenic acid (100 mg.). This melted crude at 211–221° and from dilute acetic acid gave thin yellowish plates, m. p. 224–225° alone or in admixture with the authentic *trans*-nitro acid. The neutral fraction from this reaction (100 mg.) crystallized in bold needles from acetic acid, m. p. 182–184°, and in thin plates from hexane, m. p. 182.5–183.5°. Analysis showed it to be a **trinitro-ketone**. It was not identical with either of the nitro-ketones derived from the *cis*-ketone.

Anal. Calcd. for $C_{14}H_{13}N_3O_7$: C, 50.15; H, 3.91. Found: C, 50.30; H, 3.67.

Summary

Ozonization of the hexahydrodiphenic acid of m. p. 242° yields *cis*-hexahydrophthalic acid. Ozonization of *trans*- Δ^{10} -9-keto-dodecahydrophenanthrene yields a keto-acid which can be converted into an unsaturated lactone. The latter on oxidation with permanganate gives *trans*-hexahydrophthalic acid.

Taken in conjunction with work described in the preceding papers, these facts establish the *cis*-configurations for the following substances: hexahydrodiphenic acid, m. p. 242°; perhydrodiphenic acids, m. p. 289° (*syn*) and 198° (*anti*); and the *trans*-configurations for the following: hexahydrodiphenic acid, m. p. 221°; perhydrodiphenic acids, m. p. 223° (*syn*) and 247° (*anti*).

Two additional stereochemical links between the hydrodiphenic acids and the hydrophenanthrenes have been established by the conversion

of the *cis*- and *trans*-forms of 9-keto-*as*-octahydro-phenanthrene into the corresponding nitro-hexahydro-diphenic acids.

The stereochemical implications of these results

are discussed and it is shown that they are in agreement with other, less exact, evidence.

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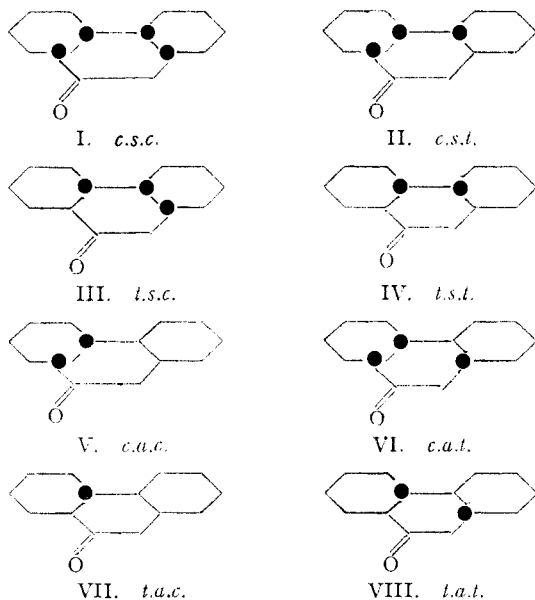
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

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

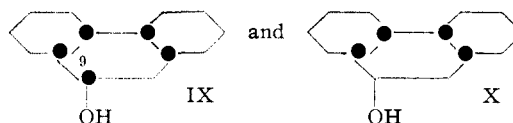
Perhydrophenanthrene can theoretically exist in six (inactive) stereoisomeric modifications.¹ Corresponding to each of four of these hydrocarbons (the *cis-syn-cis*, *trans-syn-trans*, *cis-anti-cis* and *trans-anti-trans* forms), there will be one ketone with the carbonyl group at C₉. Corresponding to each of the other two hydrocarbons (the *cis-syn-trans* and *cis-anti-trans* forms), there will be a pair of C₉ 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 enantiomeric 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.



(1) Linstead and Walpole, *J. Chem. Soc.*, 842 (1939).

This is parallel to the half esters of the perhydro-diphenic acids² 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 formulas³ to designate the configuration of the alcohols. Thus of the two possible *cis-syn-*



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 believed¹ to be 9-keto-perhydrophenanthrenes have now been shown² 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.

(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).