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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Stereochemistry of Catalytic Hydrogenation. I. The Stereochemistry of the Hydrogenation of Aromatic Rings

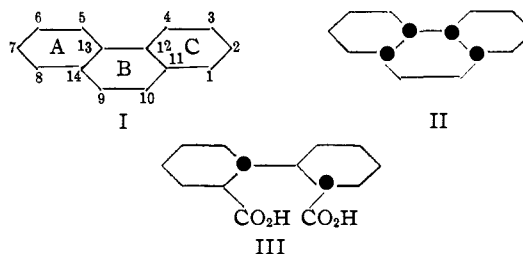
BY R. P. LINSTEAD, W. E. DOERING, SELBY B. DAVIS, PHILIP LEVINE AND RICHARD R. WHETSTONE

This paper and the six that follow it give an account of the main results which have been obtained from a stereochemical study of the catalytic hydrogenation of a number of aromatic compounds. We have examined derivatives of phenanthrene substituted in the central ring and the hydro-diphenic acids which can be obtained from them by oxidation. The key substances in the elucidation of the configuration were the perhydrodiphenic acids. The six possible isomeric forms of these have been prepared and oriented. The information so obtained has been used to orientate the hydrogenation products of the phenanthrene derivatives.

The experimental results and the determination of configuration are given in Parts II to VII. The present paper summarizes the data, and analyzes their bearing on the phenomena of catalytic hydrogenation.

The system of nomenclature for these compounds is the following.<sup>1</sup> When phenanthrene is completely hydrogenated, four (potential) asymmetric carbon atoms appear. These are numbered 11, 12, 13 and 14 in formula I. The configurations of the ring fusions AB and BC are designated *cis* or *trans* in the usual manner, according to whether the pair of hydrogen atoms on C<sub>13</sub> and C<sub>14</sub> (or C<sub>11</sub> and C<sub>12</sub>) are on the same side of the molecule. The configuration of the backbone (the C<sub>12</sub>-C<sub>13</sub> bond) is designated *syn* if the two hydrogens on

(1) Linstead, *Chemistry and Industry*, **56**, 510 (1937); Linstead and Walpole, *J. Chem. Soc.*, 842 (1939).



C<sub>12</sub> and C<sub>13</sub> are on the same side of the molecule and *anti* if they are on opposite sides. The positions of the hydrogen atoms are represented in the formulas by black dots, a dot indicating that a hydrogen atom is above the molecule. A dot is always placed on C<sub>13</sub>. On this convention, formula II represents *cis-syn-cis* (*c. s. c.*) perhydrophenanthrene. The related perhydrodiphenic acids are similarly named and represented, the molecule being written in the coiled state with the carboxyl groups together. Formula III thus represents *trans-anti-trans* (*t. a. t.*) perhydrodiphenic acid.

The catalytic hydrogenations were carried out over Adams platinum oxide in acetic acid unless otherwise stated. The following compounds were hydrogenated to the corresponding perhydro products: diphenic acid<sup>2</sup> (in alcohol as well as in acetic acid), diphenic ester,<sup>2</sup> diphenic anhydride,<sup>2</sup> *cis*-hexahydrodiphenic acid,<sup>3</sup> *trans*-hexahydrodiphenic acid,<sup>3</sup> 9-phenanthrol,<sup>4</sup> *cis-as*-octahydro-9-

(2) Linstead and Doering, *THIS JOURNAL*, **64**, 1991, 2003 (1942).

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

(4) Linstead, Whetstone and Levine, *ibid.*, **64**, 2014 (1942).

phenanthrol<sup>4</sup> (in alcohol as well), *cis*-9-keto-octahydrophenanthrene<sup>4</sup> (in alcohol), and 9,10-phenanthrenequinone.<sup>5</sup>

There is a remarkable regularity in these results. *All the hydrogenations studied have given largely cis- and syn-material.* The only compound which gives a main per-hydrogenation product containing a *trans*-linkage is the *trans*-hexahydrodiphenic acid which already contains such a linkage. The results refer to the *main* stereoisomer formed, which constitutes 75% or more of the total perhydro product. Diphenic acid both in alcohol and in acetic acid gives a small amount of the *cis-syn-trans* and *cis-anti-cis* perhydro acids. Diphenic ester gives some *anti*-material. The remaining compounds mentioned probably yield small quantities of stereoisomers containing different skeletal configurations, but these have not as yet been isolated in the pure state.

The regularity in these experiments invites a theoretical analysis. We propose three hypotheses to account for the results: (1) that when one or more aromatic rings are hydrogenated during a single period of adsorption, the hydrogen atoms add to one side of the molecule; (2) that the orientation of the adsorption of the aromatic molecule on the catalyst is affected by hindrance between the catalyst and the substrate ("catalyst hindrance"); (3) that the derivatives of diphenic acid which have been studied are hydrogenated in the coiled phase. These will now be considered in turn.

(1) **One-Sided Addition.**—Willstätter in 1908<sup>6</sup> made the basic discovery that aromatic compounds could be hydrogenated at room temperatures over a platinum catalyst. It was some years before it was observed, mainly owing to the work of Skita<sup>7</sup> and von Auwers,<sup>8</sup> that, when two or more nuclear substituents were present, the products obtained by the use of platinum were isomeric but not identical with those obtained by Sabatier hydrogenations of the same compounds over nickel at high temperatures. As is well known, it was generally accepted that the products were geometrical isomers of the von Baeyer type, the compounds prepared over platinum being *cis*, and those by the Sabatier method being *trans*. Moreover, Skita,<sup>7</sup> in particular, noted

(5) Linstead and Levine, *THIS JOURNAL*, **64**, 2022 (1942).

(6) Willstätter and Mayer, *Ber.*, **41**, 1479 (1908).

(7) Skita, *ibid.*, **53**, 1792 (1920); Skita and Schneck, *ibid.*, **55**, 144 (1922); Skita, *ibid.*, **56**, 1014 (1923); Skita, Hauber and Schönfelder, *Ann.*, **431**, 1 (1923).

(8) v. Auwers, *Ann.*, **420**, 84 (1920).

that in hydrogenations over platinum a *cis*-orientation was favored in acid media, a *trans*-orientation in neutral or basic media.

Most of the configurations of the hydrogenation products in the early work were assigned on the basis of von Auwers' generalization that, of a pair of stereoisomers of this type, the *cis*-compound has the higher density and refractive index but the lower molecular refractivity. This rule has been of considerable service, although the differences in the physical constants become slight among the more complicated molecules. For our present purpose, however, we wish to emphasize those results in which the configurations have been determined by absolute methods, depending (ultimately) on optical resolution. A number of examples of this kind are collected in Table I, which is not exhaustive. The evidence for the configuration of the product is outlined at the foot of the table, and is, in all cases, conclusive. The substances all owe their isomerism to the presence of carboxyl groups, fatty acid residues or fused rings. Compounds in which one (or more) of the orientating groups is a hydroxyl, amino or similar group have deliberately been excluded, because of the danger of stereochemical inversions in these cases.

TABLE I  
CATALYTIC HYDROGENATIONS OVER PLATINUM IN ACETIC ACID

Substance	Catalyst	Configura- tion of product	Refer- ences
1 (o-) Phthalic acid	Willstätter Pt	<i>cis</i>	9
2 Phthalic anhydride	Willstätter Pt	<i>cis</i>	9
3 Phthalimide	Willstätter Pt	<i>cis</i>	9
4 Isophthalic acid	Willstätter Pt Adams Pt	mainly <i>cis</i>	9, 10
5 Terephthalic acid	Willstätter Pt Adams Pt	<i>cis</i> + <i>trans</i>	9, 10
6 Benzene-1-acetic- 2 $\beta$ -propionic acid	Willstätter Pt	<i>cis</i>	11
7 $\beta$ -Naphthol	Skita Pt	<i>cis</i>	11
8 <i>ar</i> - $\beta$ -Tetralol	Willstätter Pt Skita Pt	<i>cis</i>	11
9 <i>ac</i> - $\beta$ -Tetralol	Willstätter Pt Skita Pt	<i>cis</i>	11
10 <i>ac</i> - $\alpha$ -Tetralol	Willstätter Pt	<i>cis</i>	11, 12
11 <i>ar</i> - $\alpha$ -Tetralol	Willstätter Pt	<i>cis</i>	11, 12
12 5-Hydroxy-hydrin- dene	Adams Pt	<i>cis</i>	13

The configuration of the products is proved by the following evidence: nos. 1-3: From the resolution of *trans*-hexahydrophthalic acid (Werner

(9) Willstätter and Jacquet, *Ber.*, **51**, 767 (1918).

(10) Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 61 (1928).

(11) Hückel, *Ann.*, **441**, 1 (1925).

(12) Hückel, Danneel, Gross and Naab, *ibid.*, **502**, 99 (1933).

(13) Cook and Linstead, *J. Chem. Soc.*, 946 (1934).

and Conrad<sup>14</sup>). No. 4: From the resolution of *trans*-hexahydro-isophthalic acid (Böeseke and Peek<sup>15</sup>). No. 5: From the work of Mills and Keats,<sup>16</sup> Nos. 6-11: From the resolution of *trans*-cyclohexane-1,2-diacetic acid (Hückel and collaborators<sup>17</sup>; Barrett and Linstead<sup>18</sup>). No. 12: From the resolution of *trans*-cyclopentane-1,2-diacetic acid (Barrett and Linstead<sup>18</sup>).

Of the twelve compounds given in Table I, all except terephthalic acid hydrogenate nearly exclusively *cis*- under these experimental conditions. It would be possible to bolster up the case by including a great deal of confirmatory evidence from hydrogenations in which the configuration of the product was known with a high degree of probability but not with certainty. However, the clear-cut evidence obtained from our studies and that presented in Table I is sufficient to demonstrate that aromatic compounds hydrogenate predominantly *cis*-, under the stated conditions. The new work summarized above is the most rigorous test of this generalization, because four asymmetric centers instead of two are involved. The generalization is restricted to the mildest type of catalytic hydrogenation, namely, that which occurs over platinum at room temperature, and in the solvent, acetic acid, which gives the most rapid addition.

This preferential addition can be explained by an application of the ideas of Farkas and Farkas.<sup>19</sup> They have shown that the catalytic hydrogenation of benzene and the exchange of hydrogen and deuterium proceed by different mechanisms. The hydrogenation involves the simultaneous addition of pairs of hydrogen atoms, whereas the exchange involves a radical or atomic reaction. Farkas and Farkas<sup>20</sup> have shown that these views can satisfactorily explain the preferential formation of *cis*-ethylenes in the half-hydrogenation of acetylenes over catalysts. It has been shown, notably by Bourguel,<sup>21</sup> that such hydrogenations yield initially *cis*-compounds but that *trans*-compounds may be formed if the hydrogenations are protracted.

In applying these conceptions to the aromatic series, we shall assume that the hydrogenation of

(14) Werner and Conrad, *Ber.*, **32**, 3046 (1899).

(15) Böeseke and Peek, *Rec. trav. chim.*, **44**, 841 (1925).

(16) Mills and Keats, *J. Chem. Soc.*, 1373 (1935); compare Malachowski and Jankiewiczówna, *Ber.*, **67**, 1783 (1934).

(17) Hückel, *et al.*, *Ann.*, **451**, 132 (1926); **518**, 155 (1935).

(18) Barrett and Linstead, *J. Chem. Soc.*, 1069 (1935).

(19) Farkas and Farkas, *Trans. Faraday Soc.*, **33**, 827 (1937).

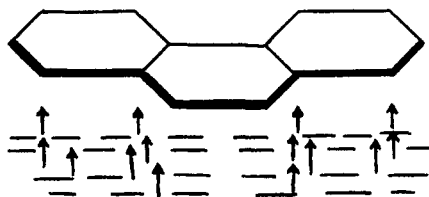
(20) Farkas and Farkas, *ibid.*, **33**, 837 (1937).

(21) Bourguel, *Bull. soc. chim.* (4), **51**, 253 (1932); *Compt. rend.*, **182**, 224 (1926).

a compound containing one aromatic ring proceeds to completion during one period of adsorption of the molecule on the catalyst surface. This assumption simplifies the argument and is in harmony with the experimental fact that benzene derivatives, except phenols, normally hydrogenate without yielding intermediates (see, for example, Vavon<sup>22</sup>). This is further connected with the fact that the hydrogenations of cyclohexene and the cyclohexadienes are exothermic.

There is an increasing body of evidence that the adsorption of an organic molecule on a catalyst, and hence the ease of hydrogenation, is affected by stereochemical considerations. The recent work of Beeck, Smith and Wheeler<sup>23</sup> has shown the importance of the orientation of the metallic atoms in the lattice of the catalyst on its activity. It is possible that the catalytic hydrogenation of large aromatic molecules, which are planar and comparatively rigid, will be determined largely by the ability of the molecule to find an area in the catalyst which has sufficient size, suitable spacing of the metallic atoms, and sufficient flatness.

We suggest that the stages in the hydrogenation which determine that the product shall have a *cis*-configuration are: (1) the adsorption of the aromatic molecule upon a suitable part of the catalyst; and (2) the addition of the hydrogen to the molecule from the underside so that all the atoms appear on the same side of the asymmetric carbon atoms. This is illustrated diagrammatically below for the case of a phenanthrene nucleus. The arrows represent the approach of the hydrogen atoms from the catalyst.



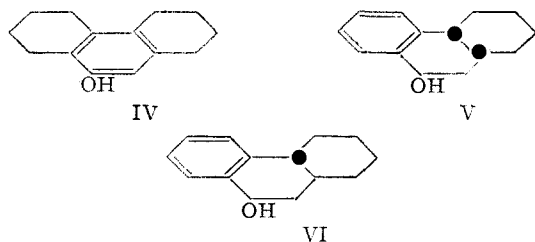
In the case of polynuclear compounds, there is little doubt that this is an oversimplification. These substances may give rise to incompletely hydrogenated compounds which are comparatively stable, of the type of tetralin. In several of the hydrogenations studied in the present work such intermediate hydrogenation products were isolated from the reaction products; for example,

(22) Vavon, *Bull. soc. chim.*, [4] **41**, 1253 (1927).

(23) Beeck, Smith and Wheeler, *Proc. Roy. Soc. (London)*, **A177**, 62 (1940).

diphenic acid yields some *cis*-hexahydrodiphenic acid and 9-phenanthrol gives the *sym*-octahydro derivative. There is no doubt, therefore, that desorption of the organic molecule from the catalyst can occur at an intermediate state of hydrogenation, and it is reasonable to suppose that some of the perhydrogenated material is formed as a result of two (or even more) separate periods of adsorption.

Consider the final stage of the hydrogenation of the *sym*-octahydrophenanthrol (IV). Simple one-sided addition of hydrogen to the remaining benzene ring would determine the configuration of all four asymmetric carbon atoms, and a *cis-syn-cis* product would be expected. The isomeric *as*-octahydro compounds (V and VI), however, do not present such a simple case. We should expect



the final hydrogenation to go *cis*- to both the *cis*-alcohol (V) and the *trans*-alcohol (VI), but the principle of one-sided addition does not enable us to predict the backbone configuration of the perhydro product. It appears equally possible for V to give a *cis-syn-cis* or a *cis-anti-cis* perhydro alcohol. The same is true of the diphenic acids, where the stable intermediate is a hexahydro acid with an unsymmetrical arrangement of hydrogen atoms. It is only possible to account for completely *cis*- and *syn*-perhydrogenation of a phenanthrene or diphenic acid derivative on the basis of the principle of one-sided addition by making the following subsidiary postulates: (1) no desorption of the molecule occurs at an intermediate stage, or (2) the intermediate which is hydrogenated in the stage which determines the configuration has double bonds at all the potential asymmetric carbon atoms. These are highly arbitrary and improbable assumptions, and a more reasonable suggestion is that a second determining factor, that of catalyst hindrance, comes into play. This is discussed later.

It has already been stated that Skita observed many cases in which *cis*-hydrogenation occurs in an acid, and *trans*- in a neutral or basic medium. It is true that the configurations of his products were often not conclusively proved, but there is

no doubt of the variability of the orientation of addition to the compounds which he studied. We have so far confined ourselves to one main set of hydrogenation conditions and have little experimental evidence to offer in this connection. A few comments may, however, be made. (1) In most of our experiments either the solvent or the molecule undergoing hydrogenation was an acid. However, *cis-as*-octahydro-9-phenanthrol and the corresponding ketone both hydrogenate *cis*- and *syn*- in a neutral (alcoholic) medium, and in the case of the phenanthrol the orientation was shown by direct comparison to be the same as that obtained in acetic acid solution. This is contrary to Skita's generalization. (2) Many of the examples studied by Skita involved the hydrogenation of phenols and aromatic amines. We think this evidence of doubtful value in relation to the stereochemistry of hydrogenation of the aromatic ring because of the possibility of the formation of hydroaromatic ketones (as has often been demonstrated experimentally) or of ketimines. These substances are capable of stereochemical inversion by enolization or an analogous process, so that the final orientation, for example, of the hydroxyl group to the methyl in a perhydrocresol, has no necessary bearing on the course of the hydrogenation of the aromatic ring.<sup>23a</sup> (3) In spite of these reservations there are a number of examples in which the acidity of the medium appears to affect the orientation of aromatic hydrogenation, and in which the orienting groups are alkyls or other groups incapable of inversion. Under suitable experimental conditions *trans*-hydrogenation can occur. It appears probable that in these reactions (and, indeed, in other cases of *trans*-hydrogenation) the mechanism of hydrogenation is different from the molecular addition involved in *cis*-hydrogenation. Atoms of hydrogen and organic radicals may well be involved, as in the exchange reactions studied by Farkas and Farkas.<sup>19</sup> The intervention of radicals is indeed strongly indicated in some of the hydrogenations of aromatic bases studied by Skita which readily yield compounds of the dicyclohexylamine type.<sup>24</sup>

Particular reference may be made to Skita's studies<sup>25</sup> of the hydrogenation of the xylenols and

(23a) With the hydrogenation of hydroaromatic ketones, which has been thoroughly studied by Vavon, Skita, Hückel and others, we are not concerned in this paper.

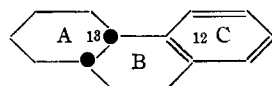
(24) Skita and Berendt, *Ber.*, **52**, 1519 (1919).

(25) Skita, *Angew. Chem.*, **34**, 230 (1921); *Ber.*, **56**, 2234 (1923).

xylylides, especially of *vic-m*-xylenol (2,6-dimethylphenol). In this case good evidence was obtained that the methyl groups in the product were oriented *trans* to each other whether the hydrogenation was carried out in a neutral or an acid medium. This not only conflicts with the run of Skita's own observations but also is opposed to the evidence summarized above and in Table I. We propose to undertake a further study of the hydrogenation of the xylenols when conditions permit. In the meantime it would seem that this is an example of the abnormal (atomic) mechanism already mentioned.

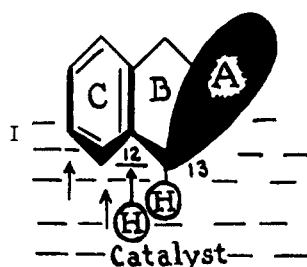
The abnormal mechanism is much more evident in hydrogenation over nickel, and may be presumed to account for the formation of predominantly *trans*-products in Sabatier hydrogenations. In the somewhat milder hydrogenations over Raney nickel the orientations are irregular, and it appears certain that both mechanisms may function. Thus we find that phenanthraquinone hydrogenates *cis-syn-cis* over platinum at 25° and almost exclusively *cis-syn-cis* over nickel at 160°. A very small amount of a *cis-syn-trans* glycol is formed under the latter conditions. On the other hand, diphenic ester can yield considerable quantities of *anti*-perhydro material over nickel,<sup>26</sup> under very similar conditions, but here the results of a number of recent experiments show considerable variations and *syn*-perhydro ester has frequently been almost the sole product.

(2) **Catalyst Hindrance.**—As was pointed out above *cis-as*-octahydro-9-phenanthrol (V), the corresponding ketone and the related *cis*-hexahydrodiphenic acid all yield *cis-syn-cis* perhydro-products. *Trans*-hexahydrodiphenic acid also undergoes *cis*- and *syn*-perhydrogenation. The simple hypothesis of one-sided addition is quite unable to account for these results, and also, as has already been pointed out, cannot explain the *cis-syn-cis* perhydrogenation of phenanthrene derivatives except on the basis of two unlikely postulates. The crux of the problem is this: Why should the position of the hydrogen on C<sub>13</sub> determine the position taken up by that which enters on C<sub>12</sub>? No explanation based on a dis-

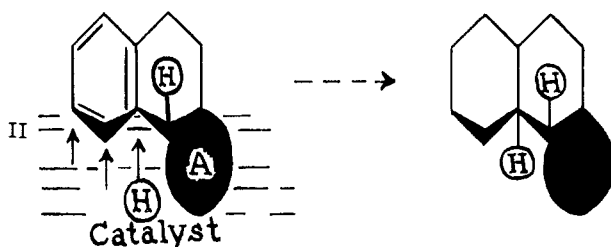


(26) Vocke, *Ann.*, **508**, 1 (1934); Linstead and Walpole, *J. Chem. Soc.*, 850 (1939).

proportionation or a migration of the hydrogens already in position can be accepted, because the integrity of the configuration already established is preserved. In our view the determining factor is one of *catalyst hindrance*, *i. e.*, a steric hindrance between the catalyst and the substrate. This is illustrated for the case of a *cis-as*-octahydrophenanthrene derivative in the diagrams given below:



Preferred adsorption; Ring A clear of catalyst; *syn*-hydrogenation occurs.



Hindrance between catalyst and ring A; adsorption inhibited; little or no *anti*-hydrogenation.

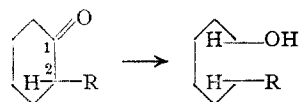
It may be taken that it is the aromatic part of the molecule which anchors it to the catalyst. Two arrangements are then possible, in which ring A is either inclined away from or toward the catalyst. In diagram I the A ring is away from the catalyst and the hydrogen atom on C<sub>13</sub> toward it. The hydrogens adding to the molecule from the underside will therefore come from the same side as the hydrogen on C<sub>13</sub>. The hydrogen atom which attaches itself to C<sub>12</sub> and determines the backbone configuration thus takes up a *syn* arrangement with respect to C<sub>13</sub>. In diagram II, the opposite state of affairs holds; ring A will be on the same side as the catalyst and any hydrogen which becomes attached to C<sub>12</sub> (by the normal mechanism) will take up the *anti*-configuration. It appears reasonable to suppose that the adsorption corresponding to I will be greatly preferred to that represented by II and therefore that *syn*-hydrogenation will preponderate. This is what is found experimentally.

The same argument can be applied to the diphenic acid derivatives, providing these sub-

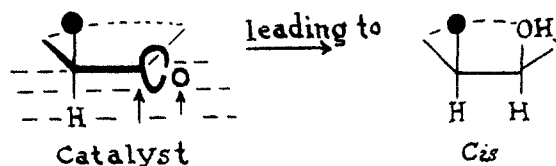
stances are considered as reacting in a coiled or "pseudo-tricyclic" state. This question is dealt with in the next section.

To the best of our knowledge, the proposal that there can be a steric hindrance between a metallic catalyst and its substrate is novel. There appears to be no other reasonable way of accounting for the regular occurrence of *syn*-hydrogenation over platinum. There is a philosophical connection with Bergmann's explanation<sup>27</sup> of the selective action of proteolytic enzymes (peptidases) on polypeptides made from natural and unnatural amino acids, respectively.

It seems probable that catalyst hindrance is a determining factor in many other reactions. Vavon has proposed<sup>28</sup> that the production of a *cis*-alcohol in the catalytic hydrogenation of substituted hydroaromatic ketones, particularly those of the ortho series, is due to a steric hindrance between the substituent group R and the entering hydrogen. This, he suggests, makes the hydrogen



attack the carbonyl double bond from the side removed from the group R, so that the hydroxyl group which is formed takes up the *cis*-position with respect to this. We agree with Vavon that steric hindrance of the group R is the operative factor but regard it as acting at an earlier stage, namely, that of adsorption. The adsorption can most readily occur with the group R inclined away from the catalyst so that the entering hydrogen on C<sub>1</sub> takes up the *cis*-position with respect to that on C<sub>2</sub>. The preferred reaction is illustrated below:



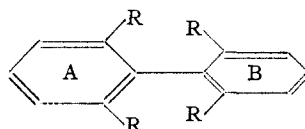
Catalyst hindrance can also account in a simple way for a remarkable discovery made by Adkins and his co-workers in 1933.<sup>29</sup> They studied the hydrogenation of various substituted diphenyls in which the rotation about the internuclear bond was restricted so that optical activity of the well-

(27) Bergmann, *Harvey Lectures*, **31**, 37 (1935-36); Bergmann and Zervas, *Z. physiol. Chem.*, **224**, 11 (1934).

(28) Vavon, *Bull. soc. chim.*, (4) **39**, 668 (1926).

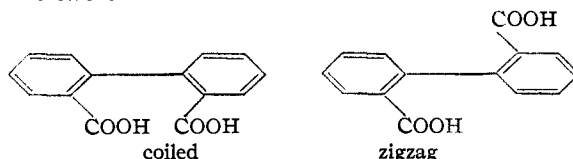
(29) Waldeland, Zartman and Adkins, *THIS JOURNAL*, **55**, 4234 (1933).

known type was possible. It was found to be quite *impossible to hydrogenate* these compounds over Raney nickel even under remarkably drastic conditions, in contrast to the comparatively easy hydrogenation of diphenyl derivatives in which free rotation was possible. We suggest that this reluctance to react originates with the fact that these restricted molecules cannot lie in one plane.



Hence if one ring lies flat on the catalyst, the other will interfere with it. Adsorption, and hence hydrogenation, is therefore inhibited. It appears that the forces which would be involved in the complete adsorption of the molecule on the catalyst are too weak to overcome the repulsion between the substituent groups R. Adkins commented upon his results in the following words: "It is possible that the same factors which prevent the rotation of the rings . . . in resolvable derivatives of diphenyl, also prevent the reaction (adsorption) of the benzenoid ring by the catalyst, and so inhibit the first step in the catalytic hydrogenation of the former." Our proposal in this connection is therefore an extension of Adkins' suggestion.

(3) **Coiling**.—A remarkable feature of the new results is that diphenic acid and its ester hydrogenate in the same stereochemical manner as do its anhydride and the phenanthrene derivatives to which it is related. The hexahydro acids also simulate their tricyclic counterparts. It is to be presumed that diphenic acid can exist in all the possible phases intermediate between the two extremes shown.



On the basis of the hypotheses already advanced, the coiled form would yield a *cis-syn-cis* perhydro-product and the zigzag form one with a *cis-anti-cis* configuration. We indeed anticipated that diphenic acid would yield a stereochemically different perhydro product from its anhydride, but this was found not to be true. Unfortunately, we have so far been unable to bring about catalytic hydrogenation of the diphenate anion in water

over platinum. The anion would be expected to exist preferentially in the zigzag form and to yield *anti*-material on hydrogenation.

As it is unlikely that the agreement of the results is purely due to coincidence, it appears that the "open-chain" derivatives of diphenic acid (the acid itself, its ester and its two hexahydrides) *all hydrogenate in the coiled or pseudo-tricyclic phase*. This would mean that this phase is the one which is most readily adsorbed on the catalyst. We can see no particular reason for this preference. Hydrogen bonding between the carboxyl groups could be invoked for the acid but not for its ester.

The hypotheses which are advanced in this paper are tentative and require additional experimental investigation from many points of view. This we hope to provide in due course. One aspect which has not yet been mentioned will have to be considered before these hypotheses could be applied generally. The present work has been almost completely confined to the ortho-substituted compounds. (This is to some extent inevitable in the study of polycyclic aromatic structures). It may be found that the behavior of compounds in which the orienting groups are further apart may be much less regular than those studied

in the present work. There are several indications in the literature that this may be true, for example, the considerable degree of *trans*-hydrogenation of terephthalic acid, as mentioned in Table I.

### Summary

The stereochemistry of the hydrogenation of a number of derivatives of diphenic acid and of phenanthrene over a platinum catalyst is discussed. The nine compounds studied all hydrogenate *cis* and *syn*.

The results are explained on the basis of three hypotheses.

1. When one or more aromatic rings are hydrogenated during a single period of adsorption, the hydrogen atoms add to one side of the molecule.

2. The orientation of the adsorption of the aromatic molecule on the catalyst is affected by hindrance between the catalyst and the substrate.

3. The open-chain derivatives of diphenic acid are hydrogenated in the coiled phase.

Earlier work is discussed in the light of these views, and certain applications to related fields are indicated.

CONVERSE MEMORIAL LABORATORY

CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 30, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Stereochemistry of Catalytic Hydrogenation. II. The Preparation of the Six Inactive Perhydrodiphenic<sup>1</sup> Acids

BY R. P. LINSTAD AND W. E. DOERING

Earlier work by Linstead and A. L. Walpole<sup>2</sup> on the hydrogenation of diphenic acid had revealed the following facts: (1) Catalytic hydrogenation of the free acid in acetic acid solution over platinum gave a perhydro acid of m. p. 273°. (2) Similar hydrogenation of dimethyl diphenate gave a solid perhydro ester, m. p. 73°, which on alkaline hydrolysis gave a perhydro acid of m. p. 220°. (3) Hydrogenation of dimethyl diphenate over Raney nickel by Adkins' procedure gave a mixture of the ester of m. p. 73° and a liquid ester which on alkaline hydrolysis gave a third perhydro acid of m. p. 244°. Other early work on the perhydro acids is reviewed later in the present paper.

(1) The common 2,2'-diphenic acid is referred to as diphenic acid for the sake of brevity throughout these papers. Its hydrogenated derivatives are correspondingly named without prefix.

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

We have now made a fuller study of the hydrogenation of diphenic acid and its derivatives over platinum, and of the stereochemical inversion of the products. This has led to the isolation of eleven distinct optically inactive hydrodiphenic acids. Six of these are dodecahydro- (perhydro-) derivatives; three are decahydro-, containing one double bond; and the remaining two are hexahydro-, and contain one intact benzene ring. This paper is concerned only with the perhydro acids.

As pointed out by Linstead and Walpole,<sup>2</sup> perhydrodiphenic acid can exist in six inactive modifications, four of which are resolvable. All the possible forms have therefore been obtained. Experiments on their resolution are described in the following paper.