

to Dr. Klaus Unna of the Merck Institute for Therapeutic Research for his coöperation on the pharmacological assays.

### Summary

Evidence is presented to show that the seeds of species of *Erythrina* contain another alkaloidal fraction besides what has been designated as the free (classical) alkaloidal fraction. This new fraction, designated the combined alkaloidal fraction, has been shown to yield on acid (preferably) or alkaline hydrolysis, a liberated alkaloidal fraction. From these liberated alkaloidal fractions of eight species of *Erythrina*, four new liberated *Ery-*

*thrina* alkaloids were isolated and characterized.

A system of nomenclature for the *Erythrina* alkaloids has been adopted, and the four new ones herein described from the liberated fractions have been named erysodine ( $C_{18}H_{21}NO_3$ ), erysopine ( $C_{17}H_{19}NO_3$ ), erysocine ( $C_{18}H_{21}NO_3$ ), and erysovine ( $C_{18}H_{21}NO_3$ ).

These four new alkaloids are all active for curare-like action on frogs.

Certain preliminary facts on the functional groups and structures of these four alkaloids have been described, and additional data will be presented in future papers.

RAHWAY, N. J.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## A New Synthesis of Coronene

BY MELVIN S. NEWMAN<sup>1</sup>

Coronene, VII, has long aroused interest not only because of its symmetric graphite-like<sup>2</sup> structure but also because the problem of its synthesis has presented a challenge to the ingenuity of the organic chemist. When Scholl and Meyer<sup>3</sup> first announced its synthesis the senior author stated that he had been occupied at intervals over a period of twenty years in attempts to prepare this hydrocarbon. Others have also mentioned attempts in this direction<sup>4</sup> and the isolation of coronene from certain coal hydrogenation residues is claimed.<sup>5</sup>

Furthermore, there are certain problems relating to the structure of polycyclic aromatic hydrocarbons which can more satisfactorily be attacked with the aid of coronene than with any other related compound.<sup>6</sup> Specifically, Professor Pauling has indicated that the values of interatomic distances can be estimated by X-ray studies and that the diamagnetic anisotropy of coronene<sup>7</sup> may be determined by making mag-

netic measurements. In both cases the symmetry of coronene should be of great value in mathematical treatment of the results.<sup>6</sup>

With these facts in mind it was decided to attempt to develop a new synthesis for coronene. The method used is illustrated by the chart.

A new method for effecting pinacolic reduction made possible the over-all conversion of 7-methyl-1-tetralone, I, to the diene, II, in 75-85% yields. This remarkably high yield in accomplishing a type of transformation usually accompanied by low yields made desirable further experiments in order to test the generality of the method: the more so since poor yields of II were obtained by methods previously reported for similar conversions.<sup>8,9</sup> The results of these experiments will be communicated shortly.

The new method consisted in adding a small amount of mercuric chloride to a benzene-absolute alcohol solution of the ketone, I, containing freshly scratched aluminum foil. On heating a vigorous reaction ensued and after three hours of refluxing the aluminum was entirely dissolved. The pinacol fraction of the products thus formed was dehydrated by boiling with acetic acid and the diene, II, crystallized on cooling.

The addition of maleic anhydride to II proceeded smoothly in boiling xylene (compare Weid-

(1) The Elizabeth Clay Howald Scholar for the year 1939-1940.

(2) By inspection of the formula it may be seen that there are two concentric hexagons of carbon atoms which are linked only to other carbons.

(3) Scholl and Meyer, *Ber.*, **65**, 902 (1932). Their synthesis is extremely difficult and indeed, it is a tribute to their skill that they succeeded at all.

(4) (a) von Braun, *ibid.*, **64**, 1787 (1931); (b) Clar and Wallenstein, *ibid.*, **64**, 2076 (1931); (c) Clar, *ibid.*, **65**, 857 (1932).

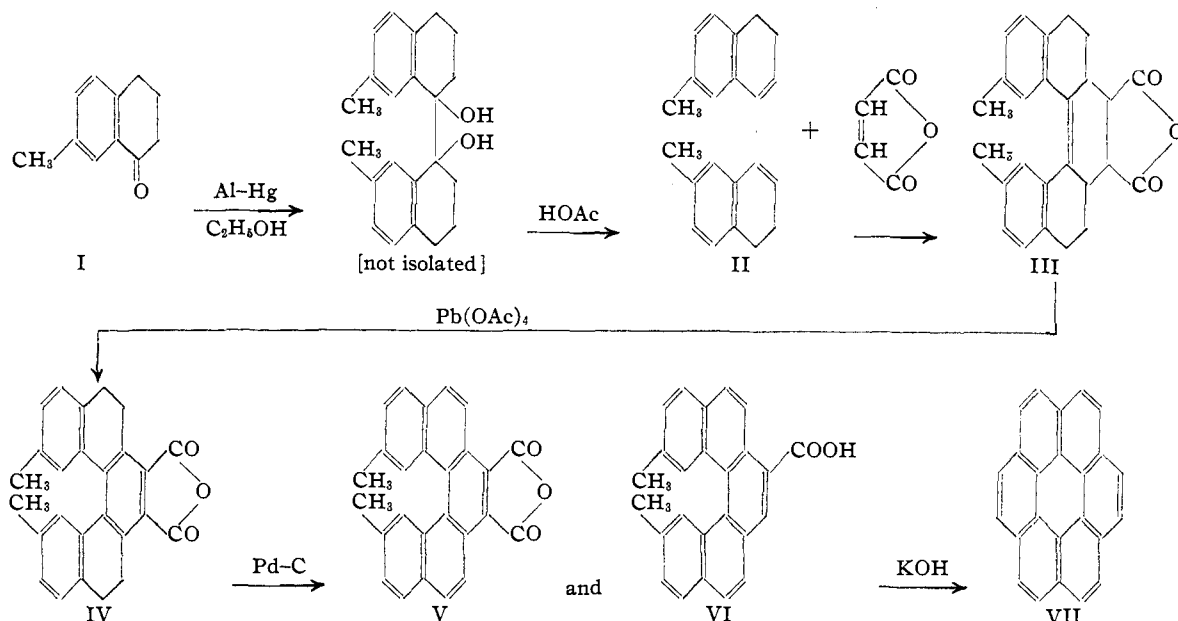
(5) French Patent 816,162, *Chem. Zentr.*, **108**, II, 3846 (1937).

(6) Communication from Professor Linus Pauling, California Institute of Technology, Pasadena, California.

(7) Pauling, *J. Chem. Phys.*, **4**, 673 (1936); see also Squire, *Compt. rend.*, **206**, 665 (1938).

(8) (a) Barnett and Lawrence, *J. Chem. Soc.*, 1104 (1935); (b) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 241 (1927); (c) Elbs and Schmitz, *J. prakt. Chem.*, **51**, 591 (1895).

(9) Weidlich, *Ber.*, **71**, 1203 (1938).

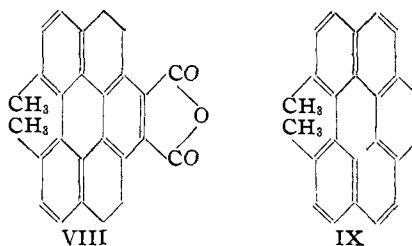


lich<sup>9</sup>) to yield a mixture of two isomeric forms of the addition product III. The more abundant of these isomers was unusual in that it could be obtained in three polymorphic modifications, the two lower melting forms being converted into the high melting form by grinding. The separation of pure compounds from this mixture proved exceedingly difficult and was accomplished only after an extended series of fractional crystallizations combined with frequent separation of crystals by hand.

Aromatization of the middle ring of III was first attempted by boiling with bromine in acetic acid, a procedure which had proved successful in an analogous case.<sup>9</sup> However, the only substance isolated was a yellow crystalline solid which contained bromine. The desired transformation was finally accomplished in good yield by treating III in acetic acid solution with two molecules of lead tetraacetate.<sup>10</sup> Since both isomers of III gave IV, the necessity for separation of these isomers was removed. However, the compound, IV, thus formed was not entirely pure for it was contaminated with a small amount of a substance which was isolated by fractional crystallization. Analysis showed this compound to contain two less hydrogen atoms than IV. Since the ready conversion of dibenzo(c,g)phenanthrene derivatives into benzo(ghi)perylene has

(10) For examples of aromatization with lead tetraacetate see Haworth, *et al.*, *J. Chem. Soc.*, 635, 643 (1935); 352, 1000 (1936); Weizmann, Bergmann and Berlin, *THIS JOURNAL*, **60**, 1331 (1938); and E. Bergmann and F. Bergmann, *ibid.* **60**, 1805 (1938).

been encountered previously,<sup>9,11</sup> it is provisionally formulated as 3,4,11,12-tetrahydro-7,8-dimethylbenzo(ghi)perylene-1,2-dicarboxylic anhydride, VIII.<sup>12</sup>



On heating IV with palladium charcoal<sup>13</sup> hydrogen was evolved and a mixture of V and VI was produced. This mixture was suitable for conversion into coronene but easily could be separated into its components by fractional recrystallization. It originally had been intended to decarboxylate and dehydrogenate V to 7,8-dimethylbenzo(ghi)perylene, IX,<sup>12</sup> according to a procedure similar to that used by Weidlich<sup>9</sup> for an analogous transformation. By heating with sulfur or selenium it was hoped that IX would yield coronene.<sup>14</sup> After many attempts at decarboxylation had failed to yield any definite products, it was found that fu-

(11) Hewett, *J. Chem. Soc.*, 1286 (1938).

(12) Nomenclature according to Patterson, *THIS JOURNAL*, **47**, 543 (1925). Only a small amount of this compound was isolated and no further work on it was done.

(13) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

(14) Instances where two appropriately located methyl groups are dehydrogenated to form a new aromatic ring are given in the following articles: Meyer and Hoffmann, *Monatsh.*, **37**, 712 (1916); Weitzenbock, *ibid.*, **39**, 310 (1918); Berger, *J. prakt. Chem.*, **133**, 339 (1932).

sion with potassium hydroxide in the range 320–360° resulted in the direct formation of coronene, VII, in small yield. After this work had been completed, an analogy for this reaction was discovered in the conversion of 2,2'-dimethyl-*meso*-naphthodianthrone to *meso*-anthrodianthrone.<sup>15</sup>

Coronene possesses an extremely high melting point, namely 437–440° cor. (lit.<sup>3</sup> 429–430° cor.). This melting point determination must be made in a sealed tube for coronene sublimes rapidly at temperatures over 400°. The purest coronene samples are only slightly darker after being melted and resolidifying but slightly impure samples become quite dark. Coronene crystallizes from dilute benzene solution in pale yellow needles, thicker needles having a brown cast. It forms a picrate (red needles) and a *sym*-trinitrobenzene derivative (orange needles) but since both of these derivatives melt with decomposition over a wide range they are not suitable for characterization.

Of special interest are the compounds V and VI. If a scale model is drawn in which the aromatic rings are in the same plane and the methyl groups occupy the same volume as in toluene, the two methyl groups would overlap considerably.<sup>16</sup> Inasmuch as these compounds must have the structures indicated (for coronene is formed from them), one (or more) of several alternatives must apply: the methyl groups may be bent back from each other but still be in the same plane as the aromatic rings; the methyl groups may be bent out of the plane of the aromatic rings; or the aromatic rings must be distorted in some way.

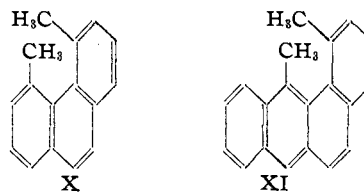
The question as to the possibility of existence and preparation of compounds in which methyl groups would interfere with each other if located at the usual valency angle with aromatic rings has been raised by Haworth and Sheldrick,<sup>17</sup> in discussing their failure to synthesize 4,5-dimethylphenanthrene, X, and by Cook and Kennaway,<sup>18</sup> in a discussion involving 1',9-dimethyl-1,2-benzanthracene, XI.

(15) Scholl and Meyer, *Ber.*, **67**, 1232 (1934); see also *Chem. Zentr.*, **99**, 11, 399 (1928).

(16) The author is indebted to Dr. E. N. Lassetre for these calculations and for valuable advice in this connection.

(17) Haworth and Sheldrick, *J. Chem. Soc.*, 1950 (1934), "... it is impossible to introduce two methyl groups in the 4,5-positions of phenanthrene without introducing excessive strain in the molecule."

(18) Cook and Kennaway, *Am. J. Cancer*, **33**, 55 (1937). "It is a little doubtful, however, whether such a hydrocarbon (*i. e.*, 1',9-dimethyl-1,2-benzanthracene, XI) could be obtained, as from stereochemical considerations, it would appear that it would be impossible to introduce two methyl groups at the positions shown without distorting at least one of the valency directions of an aromatic ring out of the plane of the ring, and such deviation has rarely, if ever, been observed."



Although compounds V and VI are not strictly analogous, they do represent examples of compounds in which considerable distortion of some sort must exist. Further discussion of this interesting problem will be deferred until the publication of work on the synthesis of a compound believed to be 4,5-dimethylchrysene, m. p. 164.0–164.8°.

### Experimental<sup>19,20</sup>

**7-Methyl-1-tetralone, I.**—This ketone was prepared according to standard methods starting from toluene and succinic anhydride.<sup>21</sup> The cyclization of  $\gamma$ -*p*-tolylbutyric acid was improved somewhat. A solution of 155 g. of acid in 250 cc. of benzene was added to 183 g. of phosphorus pentachloride. After this reaction had moderated the mixture was refluxed and then the benzene and phosphorus oxychloride were removed under reduced pressure. To a stirred solution of the acid chloride in 500 cc. of sulfur-free benzene was added 118 g. of aluminum chloride, keeping the temperature below 25° by cooling. After three hours the deep red solution was poured on ice. The desired ketone, b. p. 105–109° at 1.5–2 mm. (rapid distillation), m. p. 31–33°, was obtained in 88.5% yield.

**3,4,3',4' - Tetrahydro - 7,7' - dimethyl - 1,1' - binaphthyl, II.**—In the best experiment 42 g. of the above ketone was dissolved in 300 cc. of absolute alcohol and 200 cc. of dry sulfur-free benzene. In rapid succession were added 12 g. of freshly scratched aluminum foil<sup>22</sup> and about 0.5 g. of powdered mercuric chloride. After standing for a few minutes the flask was swirled several times and heating commenced. Within three hours the contents were almost solid with a gray precipitate. An additional 100 cc. of absolute alcohol was added and the refluxing continued for six hours. The mixture was cooled, treated with an excess of dilute hydrochloric acid, and extracted with benzene. After washing the benzene extracts with dilute acid and saturated sodium chloride solution, the solvent was distilled and the residue refluxed for two hours with 180 cc. of acetic acid to effect dehydration of the pinacol. The crystals which separated on concentrating and cooling were washed until white with cold acetic acid-petroleum ether. Additional crystals from the mother liquor brought the yield of the desired diene, II, to 30.0 g. (86%). In other runs, yields varied from 75–86%. This material was ex-

(19) All melting points corrected.

(20) The author is indebted to Mr. O. Woolfolk for aid in the preparation of several intermediates and to Mr. J. H. Walker for the analyses. Their assistance was made possible by The Ohio State W. P. A. Project 65-1-42-89.

(21) Fieser and Dunn, *This Journal*, **58**, 575 (1936); see also Ruzicka and Mörgele, *Helv. Chim. Acta*, **19**, 381 (1936).

(22) Aluminum foil  $1/64$  of an inch in thickness was secured from the Aluminum Company of America and was cut into one inch squares.

tremely difficult to free from last traces of solvent and melted from 97 to 105°. For analysis it was melted and heated at 138° for two hours, the resulting diene then melting at 110.0–111.6°.

*Anal.* Calcd. for  $C_{22}H_{22}$ : C, 92.26; H, 7.74. Found: C, 92.69, 91.96; H, 7.63, 7.55.

**1,2,2a,3,4,4a,5,6 - Octahydro - 9,12 - dimethyldibenzo(c,g)phenanthrene-3,4-dicarboxylic Anhydride, III.**—In a typical experiment a solution of 20 g. of II and 20 g. of maleic anhydride in 50 cc. of xylene was refluxed for three hours. The xylene was then removed by steam distillation and the solid was collected, dried, and crystallized from 80 cc. of acetic anhydride. The first three crops of crystals amounted to 19.6 g. (73%) and melted from 196° to 222°. By fractional crystallization from benzene combined with frequent separation of crystals by hand, there were separated two isomers of III, the more abundant of which, type A, being isolated in two polymorphic modifications, m. p. 218–220° and 231–232°. Type B melted at 226.0–226.6°. Mixtures of the isomers melted below 200°. Both modifications of type A were converted to a third form, m. p. 241–244° with decomposition, on grinding alone or mixed. This decomposition is probably due to reversal of the Diels–Alder reaction at the high temperature. If the rate of heating is slow the decomposition and melting start as low as 238°. Type A crystallized in pearly white plates of varying shape and appearance, whereas type B crystallized in clear dense prisms.

*Anal.* Calcd. for  $C_{26}H_{24}O_3$ : C, 81.22; H, 6.29. Found, type A: C, 81.00, 80.91; H, 6.37, 6.25. Type B: C, 81.32, 81.09; H, 6.33, 6.24.

**1,2,5,6 - Tetrahydro - 9,12 - dimethyldibenzo(c,g)phenanthrene-3,4-dicarboxylic Anhydride, IV.**—Treatment of III, type A, with bromine in chloroform–acetic acid according to Weidlich<sup>9</sup> resulted only in a small yield of a yellow bromine-containing substance, m. p. 217.4–219.4°.

*Anal.* Calcd. for  $C_{26}H_{18}O_3Br$ : C, 67.98; H, 4.17. Found: C, 67.69, 67.28; H, 4.15, 4.16.

Dehydrogenation of the middle ring of III was accomplished using lead tetraacetate.<sup>10</sup> Since both types of III gave identical yields of IV in this reaction, the crude mixture of crystalline addition products, III, was used in further experiments. A solution of 11.5 g. of III and 28 g. of lead tetraacetate in 40 cc. of acetic anhydride and 40 cc. of acetic acid was heated at 100° for one hour, then cooled somewhat and treated with water to incipient crystallization. The first crop of yellow crystals weighed 8.3 g. (73%) and melted at 213–224°. Recrystallization from acetic acid resulted in bright yellow needles (on rapid cooling and scratching) or in bright yellow large dense prisms (on slow cooling), both forms melting at 224–227°. A sample recrystallized four times from benzene–alcohol melted at 227.0–229.0°. Difficulty in removing last traces of solvent resulted in poor analyses.

*Anal.* Calcd. for  $C_{26}H_{20}O_3$ : C, 82.08; H, 5.30. Found: C, 81.89, 81.36; H, 5.06, 5.28.

From the mother liquor by fractional crystallization there was isolated a small amount of yellow prisms, m. p. 274–275°. This compound is presumably VIII.

*Anal.* Calcd. for  $C_{26}H_{18}O_3$ : C, 82.52; H, 4.79. Found: C, 82.43, 82.49; H, 4.76, 4.76.

**9,12 - Dimethyldibenzo(c,g)phenanthrene - 3,4 - dicarboxylic Anhydride, V, and 3-Carboxy-9,12-dimethyldibenzo(c,g)phenanthrene, VI.**—In a typical experiment 10.2 g. of IV was heated with 0.20 g. of 33% palladium charcoal<sup>13</sup> at 320–350° for ninety minutes. About 1.2 liters of hydrogen (theory 1.33 liters) was evolved. The product was dissolved in a large volume of toluene and filtered from catalyst. On concentration there crystallized 7.16 g. (71%) of a mixture of much V and a little VI. As VI was much more insoluble than V in toluene, separation was easily effected, V crystallizing in stout orange needles, m. p. 287–289°, and VI as small yellow prisms, m. p. 298–301° with decomposition.<sup>23</sup>

*Anal.* Calcd. for  $C_{26}H_{16}O_3$ : C, 82.96; H, 4.29. Found: C, 83.06, 82.90; H, 4.36, 4.30. Calcd. for  $C_{26}H_{18}O_2$ : C, 85.69; H, 5.18. Found: C, 85.71; H, 5.18.

**Coronene, VII.**—Many attempts were made to remove the carboxyl groups of V and VI in order to obtain hydrocarbons. In these experiments mixtures of V and VI were used for it was felt that similar products would be formed from each. Heating to temperatures varying from 350 to 450° with various alkaline oxides with or without metallic catalysts according to procedures described by Weidlich<sup>9</sup> and Bachmann and Kloetzel<sup>24</sup> gave mixtures from which no pure crystalline material was isolated. The direct conversion of V and VI into coronene was finally accomplished by heating with potassium hydroxide. The yield varied considerably and in some instances no coronene was obtained. Both silver and iron containers were used and the temperature of the melt was determined by a thermometer encased in a copper sheath. The best yields were in those experiments in the iron tube. In one of the best cases, 2.3 g. of a mixture of V and VI was mixed with 30 g. of potassium hydroxide and 5 cc. of water in an iron tube and was slowly heated to 320°. After ten minutes at this temperature the melt was cooled somewhat and poured cautiously into water. After almost neutralizing with acid, the insoluble material was collected, dried, and sublimed at 0.5 mm. and 380°. The pale yellow sublimate was crystallized from benzene. After two recrystallizations, the last of which was from a dilute solution, 100 mg. (5.5%) of coronene, VII, was obtained as clear long yellow needles some of which were over 1 cm. in length. The thicker crystals had a brown cast. The observations of Scholl and Meyer concerning solubility and fluorescence were confirmed. In order to take a corrected melting point a nitrogen-filled mercury thermometer (550°) was calibrated against the boiling points of diphenylamine and mercury and the freezing points of tin and zinc. Pure VII melted at 438–440° after sintering at 437°, heating being at the rate of 1° per minute. A sealed Pyrex tube was used, for coronene sublimes fairly rapidly at temperatures over 400°. On cooling it solidified and then remelted at the same temperature. The sample was very slightly discolored after these determinations.

*Anal.* Calcd. for  $C_{24}H_{12}$ : C, 95.97; H, 4.03. Found: C, 95.98, 95.71; H, 4.33, 4.30.

A deep red picrate could be prepared from coronene and picric acid in benzene but since it decomposed over a wide

(23) Determinations made in the apparatus described by Bergstrom, *Ind. Eng. Chem., Anal. Ed.*, **9**, 340 (1937).

(24) Bachmann and Kloetzel, *This Journal*, **60**, 2204 (1938).

range (250° up) on heating no analyses were made. The coronene recovered from this picrate by chromatographic adsorption on alumina was lighter in color than the original coronene but unchanged in melting point. The *sym*-trinitrobenzene derivative of coronene separated in bright orange needles from benzene but melted with decomposition over a wide range (280° up).

### Summary

A new synthesis for coronene, VII, is described. The condensation of 3,4,3',4'-tetrahydro-7,7'-dimethyl-1,1'-binaphthyl, II, with maleic anhydride yields a mixture of two isomers of 1,2,2a,3,4,4a,5,6-octahydro-9,12-dimethyldibenzo(c,g)phenanthrene-3,4-dicarboxylic anhydride, III, both of which are dehydrogenated by treatment with lead

tetraacetate to 1,2,5,6-tetrahydro-9,12-dimethyldibenzo(c,g)phenanthrene-3,4-dicarboxylic anhydride, IV. On heating with palladium charcoal, IV is further dehydrogenated to a mixture of 9,12-dimethyldibenzo(c,g)phenanthrene-3,4-dicarboxylic anhydride, V, and 3-carboxy-9,12-dimethyldibenzo(c,g)phenanthrene, VI. The fusion of V and VI with potassium hydroxide at high temperatures yields coronene, VII.

A new method for the pinacolic reduction of 7-methyl-1-tetralone, I, is described.

Compounds V and VI are discussed with regard to the spatial location of their methyl groups.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

## The Quantitative Hydrogenation of Substituted Azo Compounds with Raney Nickel at Normal Temperature and Pressure

BY W. F. WHITMORE AND A. J. REVUKAS<sup>1</sup>

### Part I. Hydrogenation and Reductive Fission

The catalytic hydrogenation of azo compounds at normal temperature and pressure over Raney nickel<sup>1a</sup> is not only of scientific interest, but also of considerable practical value. Such a method of reduction is almost an ideal one to the dyestuff analyst, since his scission products are not contaminated with other reagents. In a previous paper<sup>2</sup> it was demonstrated that both the degree of purity and the structure of a number of typical azo food dyes could be simultaneously ascertained.

The quantitative hydrogenation of an additional number of azo compounds, with potentially reducible functional groups in the aromatic nucleus, has been investigated. In the earlier work<sup>2</sup> it was shown that the nuclear substituents —CH<sub>3</sub>, —NH<sub>2</sub>, —OH, —COOH, and —SO<sub>3</sub>Na remained unaffected under the conditions employed. In the present paper it will be demonstrated that of the substituents —NO<sub>2</sub>, —CHO, —COCH<sub>3</sub>, —OCH<sub>3</sub>, and —Cl in the azo compound, only the —NO<sub>2</sub> group is directly affected under the conditions of the hydrogenation. All of the azo compounds hereinafter mentioned were

synthesized in the laboratory, since the commercially available products were often found to be of unreliable composition or purity. This publication describes a general procedure for their catalytic reduction, and the isolation and characterization of the scission products.

### Experimental Work

**Materials.**—All of the starting materials were of the purest grade available, and were purchased from the Eastman Kodak Company. Good yields of relatively pure azo products were procured by employing the customary procedures of diazotization and coupling. All of the azo compounds so prepared were recrystallized at least three times from the proper solvent, and finally dried in a vacuum desiccator, to ensure complete purity, after which they were employed in the work to be described.

**Hydrogenation Procedure.**—The accurately weighed azo compound was carefully washed into the reductor bottle with 125 ml. of solvent (95% ethanol or peroxide free dioxane). Raney nickel was then added so that the ratio of catalyst to hydrogen acceptor (azo compound) was 3 g. for each 0.01 mole. The hydrogenations were carried out at room temperature and atmospheric pressure. The apparatus utilized in the reductions was the same as that reported previously.<sup>3</sup> In general, the scission products were isolated as amine hydrochlorides by first separating the catalyst on a Büchner funnel (solution neutral) in which there was a piece of dry-ice to retard atmospheric oxidation, and then passing dry hydrogen chloride into the filtrate, purifying, and characterizing the products obtained as later described.

(1) An abstract of a thesis submitted to the faculty of the Polytechnic Institute of Brooklyn by Mr. A. J. Revukas in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(1a) Covert and Adkins, *THIS JOURNAL*, **54**, 4116 (1932).

(2) W. F. Whitmore and A. J. Revukas, *ibid.*, **59**, 1500 (1937).

(3) Whitmore and Revukas, *ibid.*, **59**, 1501 (1937).