

hours. The product was extracted with benzene, the purified benzene extract concentrated and the residue distilled at 7 mm. pressure. The fraction boiling at 191–197°, once recrystallized from alcohol, gave 19.4 g. of white crystals, m. p. 75–77° (47.5%). A sample purified by repeated recrystallization melted at 76–77° (lit.,<sup>5</sup> 77°).

*o*-Cyanotriphenylmethane (II).—A mixture of 9.85 g. of *o*-chlorotriphenylmethane, 3.88 g. of cuprous cyanide and 15 cc. of pyridine in a sealed tube was heated at 200° for forty-eight hours. The product was then decomposed with dilute ammonium hydroxide and the organic matter extracted with benzene. The benzene solution was washed with ammonium hydroxide followed by hydrochloric acid. The product was vacuum-distilled, then crystallized from alcohol yielding 7.7 g. (81%) of the nitrile, m. p. 78–82°. A sample purified by repeated crystallization melted at 82–84° (lit.,<sup>8</sup> 89°) and could not be improved by further recrystallization.

*o*-Benzoyltriphenylmethane (III, R = C<sub>6</sub>H<sub>5</sub>).—The procedure was essentially that of Seidel and Begner<sup>7a</sup> except that the hydrolysis of the imine was considerably more difficult than indicated by the German authors. It was found that even after six hours of refluxing with dilute hydrochloric acid, a small quantity of the hydrochloride was obtained unchanged. The ketone formed white needles from alcohol, m. p. 82–84°, yield 60%. A sample purified by repeated recrystallization melted at 84–86° (lit., 88<sup>7a</sup> and 84–86<sup>7b</sup>).

9,10-Diphenylanthracene (IV, R = C<sub>6</sub>H<sub>5</sub>).—(a) By the action of hydrobromic and acetic acids: the *o*-benzoyltriphenylmethane (0.5 g.), acetic acid (5 cc.) and 34% hydrobromic acid (5 cc.) were refluxed together for ten days. After cooling the mixture, the crystalline diphenylanthracene was collected and recrystallized from alcohol as light yellow plates, m. p. 245–247°; yield 0.38 g. (81%). If the reaction was interrupted at the end of four days, the yield was only 45% and a small quantity of unchanged ketone was recovered.

(b) By the action of acetic anhydride and sulfuric acid: to a solution of 0.61 g. of the ketone (III, R = C<sub>6</sub>H<sub>5</sub>) in 3 cc. of acetic anhydride, two drops of concentrated sulfuric

acid was added and the solution heated on the steam-bath for forty-five minutes to complete the reaction. The mixture was allowed to cool and the diphenylanthracene collected and washed with alcohol. The product consisted of beautiful yellow crystals with an intense bluish fluorescence, m. p. 247–248° (lit., 240<sup>8a</sup> and 248<sup>8b</sup>); yield 0.55 g. (95%). Attempts to apply this method of cyclization to *o*-benzylbenzophenone resulted in recovery of the starting material.

9-Phenyl-10-methylanthracene<sup>9</sup> (IV, R = CH<sub>3</sub>).—A Grignard reagent was prepared from 4.23 g. of methyl iodide and most of the ether distilled off. To this was added 2 g. of the nitrile in benzene (50 cc.) and the mixture was refluxed overnight. It was then decomposed with ice and ammonium chloride and the ethereal extract washed with water and sodium thiosulfate solution. The imine hydrochloride was formed by shaking the benzene solution with dilute hydrochloric acid. This precipitate was collected and refluxed for eleven days with a mixture of hydrobromic acid (20 cc.) and acetic acid (20 cc.). The product was purified by vacuum sublimation followed by crystallization from alcohol as yellow plates, m. p. 111–114°; yield 1 g. (50%). Recrystallized, it melted at 112.5–113.5° (lit.,<sup>9</sup> 113°).

9-Phenyl-10-ethylanthracene<sup>10</sup> (IV, R = C<sub>2</sub>H<sub>5</sub>).—This hydrocarbon was prepared in a manner analogous to that employed above. The nitrile (1.8 g.) was treated with a benzene solution of ethylmagnesium bromide and the hydrochloride of the resulting imine was treated as above. The product was crystallized from alcohol, m. p. 106–108°; yield 0.9 g. (47.5%). Recrystallized, it formed yellow plates with a blue fluorescence, m. p. 107–108.5° (lit.,<sup>10</sup> 110°). Despite repeated recrystallization, our melting point could not be raised further.

Anal. Calcd. for C<sub>22</sub>H<sub>18</sub>: C, 93.58; H, 6.42. Found: C, 93.70; H, 6.34.

#### Summary

The *o*-benzylphenone type of cyclization has now been extended to *o*-benzhydriphenones.

DURHAM, N. C.

RECEIVED NOVEMBER 20, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

## Reactions of Phenanthraquinone and Retenequinone with Aldehydes and Ammonium Acetate in Acetic Acid Solution<sup>1</sup>

BY EDGAR A. STECK<sup>2</sup> AND ALLAN R. DAY

The investigations of Kreps and Day<sup>3</sup> and Stein and Day<sup>4</sup> have led to formulations of the course of reactions involved in the formation of 2-substituted oxazoles from retenequinone and phenanthraquinone or the corresponding quinonimines

by reaction with aldehydes and ammonia and with aldehydes and amines. The present study represents an extension of this work to the formation of phenanthrimidazoles and retenimidazoles from phenanthraquinone and retenequinone by reaction with aldehydes and ammonium acetate in glacial acetic acid. The immediate purpose of the investigation was to determine the course of the reactions involved in imidazole formation.

(1) Presented at the Memphis meeting of the American Chemical Society in April, 1942.

(2) Present address, Winthrop Chemical Co., Rensselaer, N. Y.

(3) Kreps and Day, *J. Org. Chem.*, **6**, 140 (1941).

(4) Stein and Day, *THIS JOURNAL*, **64**, 2567, 2569 (1942).

Imidazole syntheses employing 1,2-diamino compounds are widely used, but there is little information available on the use of 1,2-diketonic types. Radziszewski<sup>5</sup> first synthesized 4,5-diphenylimidazoles by the interaction of benzil and aldehydes in alcohol solutions with dry ammonia. Davidson and co-workers<sup>6</sup> found that the yields of 4,5-diphenylimidazoles were markedly improved by using glacial acetic acid as the solvent and adding ammonium acetate or ammonium carbonate to serve as the source of ammonia. The formation of 2-substituted phenanthrimidazoles from phenanthraquinone, certain aromatic aldehydes and aqueous ammonia was first noted by Japp and Streatfield.<sup>7</sup> It must be noted, however, that Japp's method is not a general one, since oxazole formation is favored rather than imidazole formation.

It was found in the present study that when phenanthraquinone and an aldehyde were refluxed in glacial acetic acid solution containing ammonium acetate, excellent yields of 2-substituted phenanthrimidazoles resulted. Aromatic aldehydes react most readily, but the general applicability of the procedure was indicated by the preparation of 2- $\alpha$ -furfuryl- and two 2-alkylphenanthrimidazoles. The isolation of nearly quantitative yields of a number of imidazoles, uncontaminated with the corresponding oxazoles, suggested a different mechanism than that involved in oxazole formation.<sup>3,4</sup> While this work was in progress, Cook and Jones<sup>8</sup> reported the preparation of two 2-aryl phenanthrimidazoles by this method.

The reaction mixture employed, in the modification of the Radziszewski and Japp methods, involved a solution of ammonium acetate in glacial acetic acid, a system which could readily lead to acetamide formation. It was thought possible, at first, that the amide might react with the quinone as the initial step in the reaction. However, experiments showed that the amide did not react under the conditions used in this work. As a further possibility, it was assumed that the interaction of the aldehyde and acetamide might produce the necessary intermediate for the reaction. A number of aldehydes are known to react with amides in acetic acid solution to form arylidene

and arylidene bis-amides.<sup>9</sup> In order to check this assumption, benzylidene bis-acetamide was prepared. It was found not to react with phenanthraquinone and hence was eliminated as a possible intermediate. The possibility that hydrobenzamide might be formed in the reaction mixture and serve as an intermediate was eliminated by demonstrating that hydrobenzamide is unstable in hot acetic acid.

A fourth and more logical possibility was the assumption that the interaction of ammonium acetate and phenanthraquinone might produce the essential intermediate for imidazole formation. If one considers the ammonium acetate as the potential source of the elements of ammonia, the formation of a mono- or di-imine (or amine) of phenanthrene might be expected. When phenanthraquinone (I) was refluxed with ammonium acetate in glacial acetic acid, a crystalline intermediate was obtained. Furthermore, this product reacted with aldehydes in acetic acid solution to give excellent yields of 2-substituted phenanthrimidazoles. The usual reaction mixtures generally gave the imidazoles in the same yields as those obtained when the intermediate itself was isolated and used.

Analysis of this intermediate indicated it to be a di-imine triacetate or a diamine triacetate. The reactions of the compound, however, showed it to be a di-imine triacetate. On acetylation, it did not yield the known 9,10-diacetylamino-phenanthrene,<sup>10</sup> nor did it yield phenanthrazine on warming.<sup>11</sup> The di-imine (II) crystallizes from acetic acid as colorless micro-crystals, and holds three molecules of acetic acid so firmly that they are not lost after heating at 120° for several days.

The isolation of an intermediate in the reactions of phenanthraquinone, aldehydes, and ammonium acetate in acetic acid solution permits a formulation of the course of reaction for imidazole formation under these conditions. The initial reaction is the formation of the 9,10-phenanthraquinone di-imine (II). The latter then undergoes an aldol-type of condensation with the aldehyde to form the intermediate (III). This is followed by two hydrogen shifts to form (IV) and subsequent loss of water to form the imidazole (V). The initial condensation is undoubtedly an

(5) Radziszewski, *Ber.*, **15**, 1493, 2706 (1882); **16**, 487, 747 (1883).

(6) Davidson, *J. Org. Chem.*, **2**, 319 (1937).

(7) Japp and Streatfield, *J. Chem. Soc.*, **41**, 146 (1882).

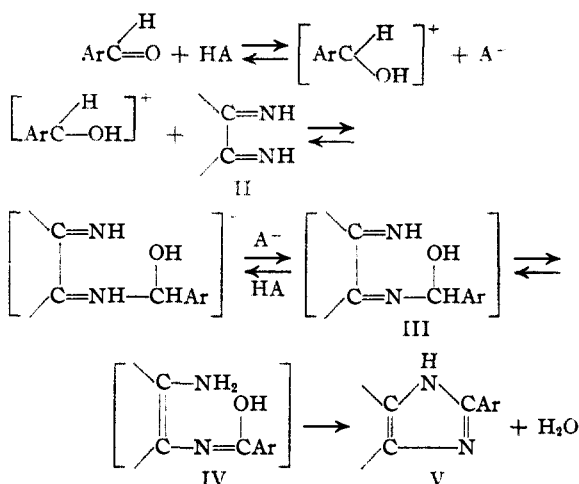
(8) Cook and Jones, *ibid.*, **282** (1941).

(9) Noyes and Forman, *THIS JOURNAL*, **56**, 3493 (1933); Pandya, *Proc. Indian Acad. Sci.*, **7A**, 351, 376 (1938); **10A**, 279, 282, 285 (1939); **14A**, 18 (1941).

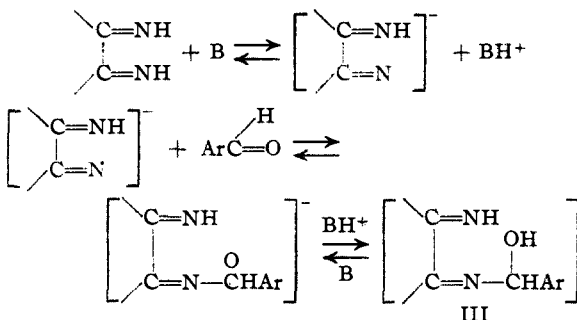
(10) Pschorr, *Ber.*, **35**, 2739 (1902).

(11) Schiedt, *J. prakt. Chem.*, [2] **157**, 220 (1941).

acid catalyzed reaction and the course of the reaction may be formulated as



It was found that the di-imine also condenses with aldehydes to form 2-substituted phenanthrimidazoles under the influence of sodium hydroxide or piperidine. Under the catalytic influence of bases, the formation of III may be formulated as follows



This reaction, which was so successful for the preparation of 2-substituted phenanthrimidazoles, was studied further as a possible method for the preparation of the corresponding retenimidazoles. Only two retenimidazoles have been reported in the literature,<sup>8</sup> hence a general method should be of some interest. When retenequinone was heated with ammonium acetate in glacial acetic acid, a compound was formed which at first was thought to be a di-imine intermediate similar to the one obtained from phenanthraquinone. Analyses, however, showed that it could not be a di-imine. The analytical values suggested it might be aminoretenol, but the formation of such a compound, under the experimental conditions used, is improbable. This derivative was eliminated as an intermediate for imidazole formation when it was found that it did not react

with benzaldehyde either in the presence of acetic acid or in the presence of bases.

It is interesting to note that good yields of imidazoles resulted when retenequinone, aldehydes, and ammonium acetate were heated in acetic acid solution. It is probable that retenequinone di-imine is the necessary intermediate in these reactions, even though it could not be isolated. Retenimidazole was obtained by heating the quinone, hexamethylenetetramine, and ammonium acetate in acetic acid solution. 2-Phenylretenimidazole was prepared from a similar reaction, using benzaldehyde. With salicylaldehyde, a mixture of 2-(2'-hydroxyphenyl)-retenoxazole and 2-(2'-hydroxyphenyl)-retenimidazole was obtained, with the former predominating. This is a surprising result in view of the fact that phenanthraquinone yielded only the corresponding imidazole in this reaction. There is no explanation for this anomalous behavior at the present time.

### Experimental

**New Compounds.**—All new compounds are indicated by (NC) immediately following the name. All of the melting points are corrected values.

**Preparation of Phenanthraquinone.**—The directions of Graebe<sup>12</sup> were modified, in that the purification through the use of sodium bisulfite was carried out according to Courtot.<sup>13</sup> The crude quinone was recrystallized from 50% acetic acid; yields 55–62%; m. p. 208–209.5°.

**Reactions of Phenanthraquinone in Glacial Acetic Acid. Phenanthraquinone and Acetamide.**—No reaction was observed when these compounds were heated in glacial acetic acid. The quinone was recovered quantitatively.

**Phenanthraquinone and Benzylidene Bisacetamide.**—Benzylidene bisacetamide was prepared according to Noyes and Forman<sup>9</sup>; m. p. 254°.<sup>14</sup>

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: N, 13.59. Found: N, 13.49.

No reaction occurred when benzylidene bisacetamide and the quinone were refluxed in glacial acetic acid for one hour. The quinone was recovered quantitatively.

**Phenanthraquinone and Ammonium Acetate. Preparation of Phenanthraquinone Di-imine Triacetate (NC).**—A solution of 4 g. (0.0192 mole) of phenanthraquinone and 30.6 g. (0.40 mole) of ammonium acetate in 55 cc. of glacial acetic acid was refluxed for one hour, although solid began to separate in ten minutes. The product was collected and washed with 3:1 ethyl acetate–acetic acid and dried; yield, 3.8–4 g.; m. p. 290–292°. A sample recrystallized from glacial acetic acid melted at 243–244°. Analysis of this sample indicated 4 moles of acetic acid.

*Anal.* Calcd. for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>·4CH<sub>3</sub>COOH: N, 6.28. Found: N, 6.48, 6.32.

(12) Graebe, *Ann.*, **167**, 140 (1873).

(13) Courtot, *Ann. chim.*, [10] **14**, 69 (1930).

(14) Noyes and Forman reported m. p. 238°.

The purified sample lost one mole of acetic acid when dried at 120°, for several days; white micro crystals, m. p. 240–250°. Titration of the bound acid with standard alkali was carried out in the presence of phenolphthalein. Calcd. for triacetate: 46.6. Found: 45.90. *Anal.* Calcd. for  $C_{14}H_{10}N_2 \cdot 3CH_3COOH$ : C, 62.18; H, 5.71; N, 7.26. Found: C, 62.01, 62.26; H, 5.66, 5.81; N, 7.31, 7.33.

The diacetyl derivative (NC) of the di-imine was prepared by heating a sample of the di-imine triacetate with acetic acid and acetic anhydride. Creamy white needles were obtained by recrystallization from dioxane and water; m. p. 259–260°. Pchorr<sup>10</sup> reported 330° for the corresponding 9,10-diacetylaminophenanthrene.

*Anal.* Calcd. for  $C_{18}H_{14}N_2O_2$ : N, 9.66. Found: N, 9.72.

**Reaction of Phenanthraquinone Di-imine Triacetate with Benzaldehyde.** (a) **In Glacial Acetic Acid.**—A mixture of 0.50 g. (0.0013 mole) of the di-imine triacetate and 0.2 g. (0.0019 mole) of benzaldehyde in 30 cc. of glacial acetic acid was refluxed for one hour. On cooling an 85% yield of the 2-phenylphenanthrimidazole was obtained. Evaporation of the filtrate brought the yield to 97%. The product was recrystallized from pyridine and water; fine colorless plates; m. p. 314°, picrate, m. p. 289–290°.

*Anal.* Calcd. for  $C_{21}H_{14}N_2$ : N, 9.55. Found: N, 9.67.

(b) **In the Presence of Sodium Hydroxide.**—One gram (0.0026 mole) of the di-imine triacetate was suspended in absolute alcohol and made alkaline by the addition of a solution of sodium hydroxide in absolute alcohol. Then 0.34 g. (0.0032 mole) of benzaldehyde was added and the mixture refluxed for one hour, cooled and filtered. Evaporation of the filtrate gave more 2-phenylphenanthrimidazole; yield, 87%. A sample was recrystallized from pyridine and water, m. p. 314°.

(c) **In the Presence of Piperidine.**—One gram of the di-imine triacetate and 0.34 g. of benzaldehyde in 6 cc. of piperidine were heated on the water-bath for one hour. On dilution with water a 60% yield of 2-phenylphenanthrimidazole was obtained. A sample recrystallized from pyridine and water melted at 314°.

**General Procedure for the Preparation of 2-Substituted Phenanthrimidazoles.**—A solution of 2.08 g. (0.01 mole) of phenanthraquinone and 15.5 g. (0.2 mole) of ammonium acetate in hot glacial acetic acid was treated with 0.01–0.014 mole of the appropriate pure aldehyde in 10 cc. of glacial acetic acid and the reaction mixture then refluxed for one hour, unless the separation of large amounts of solid prevented it. The cooled mixture was filtered and the filtrate diluted with 150 cc. of water. Neutralization of the diluted filtrate with ammonium hydroxide, in some cases, precipitated more of the imidazole. The combined precipitates were washed with water, dried and recrystallized from alcohol, acetone, benzene or pyridine, after treatment with Darco in the same solvent; crude yields, 88–98%, pure yields, 80–90%. Since a number of the compounds hold solvents firmly, they were dried at 115–135°.

Several of the following imidazoles were prepared by the direct action of the aldehyde on the di-imine triacetate in acetic acid solution. The yields were equally good but the method is less convenient than the one described above.

**Phenanthrimidazole (NC).**—Hexamethylenetetramine (2.8 g., 0.02 mole) was used as the source of formaldehyde. The product was recrystallized from alcohol and water; colorless micro crystals; m. p. 292°.

*Anal.* Calcd. for  $C_{16}H_{10}N_2$ : C, 82.53; H, 4.63; N, 12.85. Found: C, 82.70; H, 4.89; N, 12.80.

**2-Isopropylphenanthrimidazole (NC).**—The isobutyraldehyde used for this experiment was distilled just before using. The crude imidazole was recrystallized from alcohol and water; colorless, micro crystals; m. p. 228–229°.

*Anal.* Calcd. for  $C_{18}H_{18}N_2$ : C, 83.00; H, 6.21; N, 10.77. Found: C, 83.03; H, 6.16; N, 10.69.

**2- $\alpha$ -Furfurylphenanthrimidazole (NC).**—Freshly distilled furfuraldehyde (b. p. 158–159°) was used for this preparation. The product was recrystallized from pyridine and water; colorless needles; m. p. 279.5–280.5°.

*Anal.* Calcd. for  $C_{19}H_{12}N_2O \cdot H_2O$ : C, 75.45; H, 4.68; N, 9.27. Found: C, 75.59; H, 4.70; N, 9.36.

**2-Phenylphenanthrimidazole.**—The crude product was recrystallized from pyridine and water; m. p. 314°.

**2-(2'-Hydroxyphenyl)-phenanthrimidazole.**—The use of salicylaldehyde produced this imidazole. It was recrystallized from pyridine and water and dried at 135°; m. p. 287–287.5°.<sup>15</sup>

*Anal.* Calcd. for  $C_{21}H_{14}N_2O \cdot \frac{1}{2}H_2O$ : N, 8.80. Found: N, 8.78, 8.82.

**2-(3'-Hydroxyphenyl)-phenanthrimidazole (NC).**—*m*-Hydroxybenzaldehyde was used in this case. The crude imidazole was recrystallized from alcohol and water, colorless needles, m. p. 343–344°.

*Anal.* Calcd. for  $C_{21}H_{14}N_2O$ : C, 81.24; H, 4.23; N, 9.03. Found: C, 80.96; H, 4.11; N, 9.09.

**2-(4'-Hydroxyphenyl)-phenanthrimidazole.**—The crude product from the use of *p*-hydroxybenzaldehyde was recrystallized from pyridine and water; m. p. above 360°.

*Anal.* Calcd. for  $C_{21}H_{14}N_2O$ : N, 9.03. Found: N, 9.01.

**2-(2'-Methoxyphenyl)-phenanthrimidazole.**—Aldehyde used, *o*-methoxybenzaldehyde. The crude imidazole was recrystallized from benzene and alcohol (2:1); colorless needles; m. p. 214–215°.<sup>16</sup>

*Anal.* Calcd. for  $C_{22}H_{16}N_2O$ : N, 8.62. Found: N, 8.57.

**2-(4'-Methoxyphenyl)-phenanthrimidazole (NC).**—Aldehyde used, anisaldehyde. The product was recrystallized from alcohol and water; colorless, micro crystals; m. p. 254–255°.

*Anal.* Calcd. for  $C_{22}H_{16}N_2O$ : C, 81.43; H, 4.98; N, 8.62. Found: C, 81.27; H, 5.07; N, 8.67.

**2-(3'-Nitrophenyl)-phenanthrimidazole.**—Aldehyde used, *m*-nitrobenzaldehyde. The crude imidazole was recrystallized from pyridine and water; yellow needles; m. p. 271.5–272°.<sup>17</sup>

*Anal.* Calcd. for  $C_{21}H_{13}N_3O_2$ : N, 12.47. Found: N, 12.60.

(15) Japp and Streatfield reported 270–276°.

(16) Japp and Streatfield reported yellow needles, m. p. 207–208.5°.

(17) Sircar and Sircar (*J. Chem. Soc.*, 123, 1561 (1923)) reported m. p. 240°.

**2-(4'-Nitrophenyl)-phenanthrimidazole (NC).**—Aldehyde used, *p*-nitrobenzaldehyde. The imidazole was recrystallized from pyridine and water; orange needles, m. p. 341°.

*Anal.* Calcd. for  $C_{21}H_{12}N_2O_2$ : C, 74.27; H, 3.87; N, 12.47. Found: C, 74.39; H, 4.01; N, 12.58.

**2-(2'-Chlorophenyl)-phenanthrimidazole (NC).**—Aldehyde used, *o*-chlorobenzaldehyde. The product was recrystallized from acetone and water; colorless needles, m. p. 235–235.5°.

*Anal.* Calcd. for  $C_{21}H_{13}N_2Cl$ : C, 76.69; H, 4.00; N, 8.53. Found: C, 76.48; H, 4.08; N, 8.49.

**2-(4'-Dimethylaminophenyl)-phenanthrimidazole (NC).**—Aldehyde used, *p*-dimethylaminobenzaldehyde. The product was recrystallized from pyridine and water; yellow plates, m. p. 259–260°.

*Anal.* Calcd. for  $C_{23}H_{19}N_3$ : C, 81.85; H, 5.69; N, 12.44. Found: C, 81.81; H, 5.48; N, 12.39.

**2-(3',4'-Methylenedioxyphenyl)-phenanthrimidazole (NC).**—Aldehyde used, piperonal. The crude imidazole was recrystallized from pyridine and water; colorless needles, m. p. 257–257.5°.

*Anal.* Calcd. for  $C_{22}H_{14}N_2O_2$ : C, 78.88; H, 4.18; N, 8.29. Found: C, 78.80; H, 4.28; N, 8.32.

**Reaction of Retenequinone with Ammonium Acetate in Glacial Acetic Acid.**—A solution of 3 g. (0.011 mole) retenequinone in 50 cc. of hot glacial acetic acid was treated with 18 g. (0.23 mole) of ammonium acetate and the solution refluxed for one hour. Evaporation of the solution or the addition of water gave high yields of a crystalline compound. The product was recrystallized from 1:1 acetic acid–ethyl acetate; colorless needles, m. p. 211–220°. The pure product darkens gradually on standing. The analytical values agree fairly well with the calculated values for aminoretenol, but its formation under the above conditions is improbable.

*Anal.* Calcd. for  $C_{13}H_{13}NO$ : C, 81.51; H, 7.20; N, 5.17. Found: C, 81.86; H, 6.91; N, 5.21.

The picrate, recrystallized from acetone and water, melted at 226–227°.

*Anal.* Calcd. for  $C_{24}H_{22}N_4O_3$ : C, 58.27; H, 4.50. Found: C, 58.48; H, 5.02.

When the compound was refluxed with benzaldehyde in glacial acetic acid, no reaction occurred and it was recovered quantitatively.

**Retenimidazole (NC).**—Retenequinone was treated with ammonium acetate and hexamethylenetetramine in glacial acetic acid, as described under phenanthraquinone. The product was recrystallized from acetone and water; colorless prisms. The compound melted at 128–132°, resolidified and then remelted at 167–168°.

*Anal.* Calcd. for  $C_{19}H_{18}N_2O \cdot H_2O$ : C, 78.02; H, 6.91; N, 9.58. Found: C, 77.85; H, 6.75; N, 9.73.

**2-Phenylretenimidazole (NC).**—Aldehyde used, benzaldehyde. The crude imidazole was recrystallized from dilute acetic acid from which it was obtained as its acetate; colorless needles, m. p. 93–100°.

*Anal.* Calcd. for  $C_{25}H_{22}N_2 \cdot CH_3COOH$ : C, 78.98; H, 6.40; N, 6.83. Found: C, 78.86; H, 6.55; N, 6.78.

**2-(2'-Hydroxyphenyl)-retenoxazole and 2-(2'-Hydroxyphenyl)-retenimidazole.**—When retenequinone was treated with ammonium acetate and salicylaldehyde in acetic acid, a mixture of oxazole and imidazole was formed. The product was fractionated from dioxane and the least soluble fraction was recrystallized from alcohol; colorless needles of the oxazole, m. p. 243–244°; yield 65%.

*Anal.* Calcd. for  $C_{25}H_{21}NO_2$ : N, 3.81. Found: N, 3.91.

The more soluble fraction in the dioxane was recrystallized from 65% alcohol; colorless needles of the imidazole, m. p. 216–217°, yield 32%.

*Anal.* Calcd. for  $C_{25}H_{23}N_2O$ : N, 7.65. Found: N, 7.64.

### Summary

1. The reactions of phenanthraquinone and retenequinone with aldehydes and ammonium acetate in glacial acetic acid have been studied. A series of 2-substituted phenanthrimidazoles and retenimidazoles have been prepared.

2. It has been shown that the probable intermediate for imidazole formation is a quinone-dimine. The latter undergoes an aldol type of condensation with aldehydes, followed by two shifts of hydrogen and subsequent ring closure to the imidazole. The aldol-type condensation noted above is susceptible to both acidic and basic catalysts.

PHILADELPHIA, PA.

RECEIVED DECEMBER 1, 1942