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# UNSYMMETRICAL PHENANTHRIDONES. I. THE SYNTHESIS OF 2-NITRO- AND OF 7-NITROPHENANTHRIDONE

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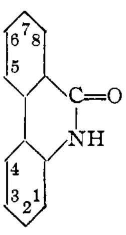
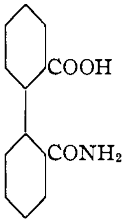
Although first synthesized in 1893, the unusually stable ring system called phenanthridone (I) has been very little studied. Two papers from Graebe's Laboratory not only furnish the two most important syntheses, but most of the knowledge of the reactions of this rather inert substance. The first synthesis[2] involved the action of alkaline sodium hypobromite upon diphenamic acid (II) and has recently been repeated in two other Laboratories.[3] The second[4] reported that "almost quantitative" yields of phenanthridone could be obtained by fusion of 4-aminofluorenone (III) with potassium hydroxide.



I



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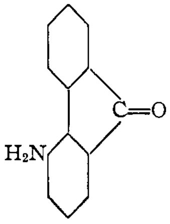

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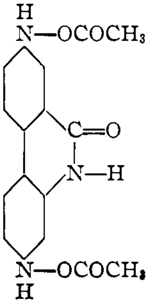

IV

The entire literature of phenanthridone up to January 1, 1926, is completed by six other papers,[5] which report various less satisfactory methods of synthesis but no further reactions of importance.

The literature of phenanthridone derivatives has been rendered meager because of the alleged unreactiveness of the parent material. Thus no substitution products have been reported save 2,7-N-diacetylamino-

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[1] This paper is constructed from a portion of a thesis submitted by E. H. Huntress to the Faculty of the Massachusetts Institute of Technology in January, 1927, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Owing to the death of Professor Moore, the junior author assumes responsibility for the statements in this article.

[2] Graebe and Wander, *Ann.*, **276**, 245 (1893).

[3] (a) Oyster and Adkins, THIS JOURNAL, **43**, 208 (1921). (b) Underwood and Kochmann, *ibid.*, **46**, 2073 (1924).

[4] Graebe and Schestakow, *Ann.*, **284**, 312 (1895).

[5] (a) Pictet and Patry, *Ber.*, **26**, 1964 (1893). (b) Pictet and Hubert, *Ber.*, **29**, 1188 (1896). (c) Pictet, *Chem.-Ztg.*, **18**, 1822 (1894). (d) Kerp, *Ber.*, **29**, 230 (1896). (e) Pictet and Gonset, *Arch. sci. phys. nat.*, [4] **3**, 37 (1897); *Chem. Centr.*, [1] **68**, 413 (1897). (f) Meyer and Hofmann, *Monatsh.*, **37**, 701 (1916).

phenanthridone (IV),[6] and this was synthesized by a process which did not involve direct substitution in the phenanthridone nucleus. The structure of two phenanthridone analogs in the naphthalene series has been studied by Graebe[7] and the literature of derivatives is completed by six dyes,[8] whose structures have been assumed from their mode of synthesis and intermediates. Thus it appears that no simple unsymmetrically substituted phenanthridones have been examined. The work reported in this paper represents the beginning[9] of a study of the extent to which the unusual unreactivity and stability of phenanthridone may be modified by unsymmetrical substitution.[10]

The mononitrophenanthridones were selected as the first class to be studied. Of the eight possible monosubstitution products we particularly desired the 2-nitro and 7-nitro isomers for comparison with the products obtained in another investigation. In pursuit of the desired substances we have essayed their preparation in three ways: (1) by alkaline fusion of 7-nitro-4-aminofluorenone, (2) by direct nitration of phenanthridone, and (3) by the action of alkaline hypobromite upon the corresponding nitrodiphenamic acids.

1. **Alkaline Fusion of 7-Nitro-4-aminofluorenone.**—The first mode of attack was analogous to that which gave Graebe and Schestakow excellent yields of phenanthridone. The sequence of steps employed is best indicated in the diagram on the following page.

After effecting profound improvement in the published method for preparing 4-nitrodiphenic acid (V), we found that heating the product with concd. sulfuric acid gave a quantitative yield of only one of two possible condensation products. 7-Nitrofluorenone-4-carboxylic acid (VI) was thus formed by ring condensation of that carboxyl group in the *meta* position to the nitro group. The structure of this new nitroketo acid was established by oxidation to hemimellitic acid, a result in consonance only with the assigned configuration. This ring formation from 4-nitrodiphenic acid is in sharp contrast with the recorded failure[3b] of the corresponding symmetrical 4,4′-dinitrodiphenic acid to give a keto acid derivative. Because preparation of phenanthraquinone and isolation of its 2-nitro derivatives proved tedious preludes to the synthesis of 4-nitrodiphenic acid and its condensation, we have devised a method for pre-

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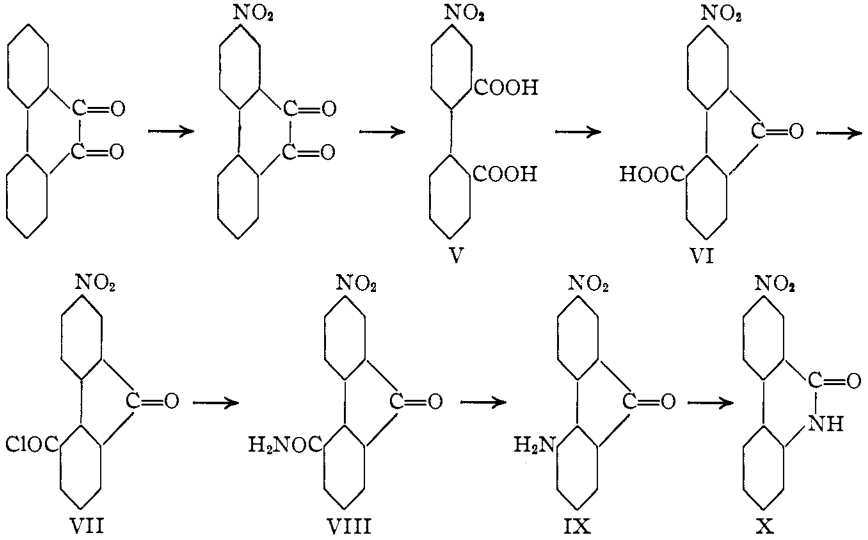
[6] Adkins, Steinbring and Pickering, This Journal, **46**, 1922 (1924).

[7] Graebe, *Ann.*, **335**, 124 (1904).

[8] Ger. pat. 236,857 (1911); *Chem. Zentr.*, [II] **82**, 323 (1911). Brass and Heide, *Ber.*, **57**, 120 (1924).

[9] The research begun in collaboration with the late Professor Moore is being continued by the writer in this Laboratory.

[10] Phenanthridone itself is unsymmetrical in the strict sense, but our use of the term implies that the —C=O and >NH groups may be considered equivalent in order to emphasize the analogy with phenanthraquinone.



paring 7-nitrofluorenone-4-carboxylic acid by direct nitration of fluorenone-4-carboxylic acid. Since the latter is readily prepared in quantitative yield from easily accessible[11] diphenic acid and its nitration gives excellent yields, our progress has been much facilitated by this development. By oxidation of the principal nitration product to hemimellitic acid, and by mixed-melting-point comparisons of the nitro acid and its methyl ester with the corresponding product from the other process, we have conclusively demonstrated that it is indeed 7-nitrofluorenone-4-carboxylic acid.

By the conventional reaction with phosphorus pentachloride we obtained nearly complete conversion of 7-nitrofluorenone-4-carboxylic acid to its chloride (VII). This in turn gave quantitative yields of amide (VIII) after treatment with ammonia. Conversion of this amide to 7-nitro-4-aminofluorenone (IX) by means of the Hofmann reaction, however, offered considerable difficulty because the formation of a troublesome by-product diverted much material from reaction in the desired sense. Although on small-scale experiments we finally raised the yield to 56%, larger runs averaged only 28% and we were unable to improve this figure. While the original 7-nitroketo acid, its chloride and amide all formed yellow crystals, the nitro-aminoketone possessed a brilliant scarlet color. Its mono-acetyl derivative, however, proved to be brilliant yellow. We are not acquainted with any similar case in which acetylation produces such profound color change.

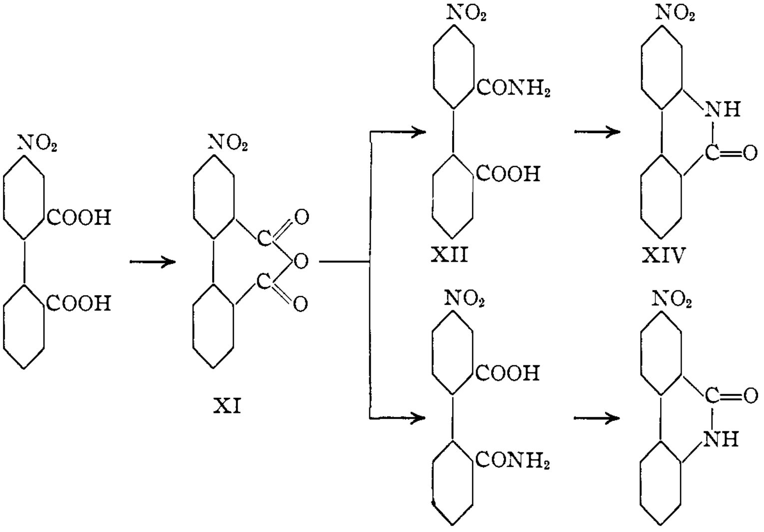
All attempts to obtain 7-nitrophenanthridone (X) by fusion of this red amine with alkali led only to the formation of a black, acidic, infusible,

[11] Huntress, "Organic Syntheses," John Wiley and Sons, New York, **1927**, vol. **7**.

vitreous substance of undetermined constitution. We later found that 7-nitrophenanthridone is destroyed under the conditions of the fusion.

2. **Nitration of Phenanthridone.**—By direct nitration of phenanthridone we obtained two nitration products which possessed very different solubilities and could be separated with alcohol. Although analysis showed that both the materials were mononitrophenanthridones, we found that neither corresponded either to the 2-nitro or 7-nitro isomers. Their specific characterizations, therefore, have been deferred to a later paper.

3. **Synthesis of 2-Nitro- and of 7-Nitrophenanthridone from the Two Isomeric 4-Nitrodiphenamic Acids.**—This third and successful method was an extension of the process used by Graebe[2] for the original synthesis of phenanthridone and may be represented as follows.



For the first stage of this process we devised a procedure which gave practically quantitative yields of pure 4-nitrodiphenic anhydride. Although this substance proved very reactive and readily hydrolyzed in the presence of moisture, its relative ease of preparation is in contrast to the behavior of the corresponding symmetrical 4,4′-dinitrodiphenic acid, which has repeatedly failed[3b,12] to yield the expected dinitrodiphenic anhydride even under extreme conditions.

When 4-nitrodiphenic anhydride is treated with concd. ammonium hydroxide at a low temperature, addition of ammonia to the ruptured anhydride linkage occurs in both possible senses, yielding approximately equal quantities of two isomeric 4-nitrodiphenamic acids. These two materials are so much alike in properties, and separate so sluggishly from

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[12] Schmidt and Kämpf, *Ber.*, **36**, 3743 (1903).

solvents, that their separation proved difficult. By a laborious fractional crystallization from alcohol, however, we have obtained pure samples of the two substances.

The structures of the high-melting 4-nitro-2-diphenamic acid (XII) and the low-melting 4-nitro-2′-diphenamic acid (XIII) follow from those of 2-nitro- (XIV) and 7-nitrophenanthridone (X) which they give, respectively, in good yield upon treatment with alkaline hypobromite. By analysis of the two products so obtained, we have definitely characterized them as phenanthridones and sharply distinguished them from the amino acids which would have resulted from opening of the heterocyclic ring. By degradative oxidation of the high-melting nitrophenanthridone with alkaline potassium permanganate, we obtained nitric acid and *o*-phthalic acid, a result consistent only with the structure of 2-nitrophenanthridone. Since by reason of their method of preparation from 4-nitrodiphenic anhydride, only the 2-nitro and 7-nitro isomers could result, it follows that the low-melting isomer is 7-nitrophenanthridone.

## Experimental Part

### 1. Preparation of 7-Nitro-4-aminofluorenone

**Phenanthraquinone.**—We employed the general procedure of Underwood and Kochmann,[3b] oxidizing in each run 200 g. of crude "80%" phenanthrene with 1200 g. of potassium dichromate dissolved in a solution of 1 liter of concd. sulfuric acid in 3 liters of water. We found that the use of pure sodium bisulfite solution is essential for extraction of the crude oxidation product, that extraction for more than half an hour diminishes the yield, and that after the powdered, crude material has once been extracted with 2.5 liters of sodium bisulfite solution containing 200 g. of the salt per liter, the additional product obtained by subsequent extractions is not worth the trouble required; yield, 70 g., or 37%; m. p., 202–203° (206–207°, corr.).

**2-Nitrophenanthraquinone.**—Following Schmidt and Spoun,[13] we obtained 42.5% of 2-nitrophenanthraquinone; m. p., 257–258° (uncorr.).

**4-Nitrodiphenic Acid.**—Ten g.[14] of pure 2-nitrophenanthraquinone, dissolved in 30 cc. of pure concd. sulfuric acid, was run into 100 cc. of water with vigorous agitation.[15] After adding a hot solution of 40 g. of potassium dichromate in 400 cc. of water, the container was arranged for motor stirring without condenser and vigorously agitated for two and one-half hours at the boiling point. After standing cold for several hours the product was filtered and washed free from chromate. The crude acid was then dissolved in the minimum quantity of cold water by gradual addition of solid sodium bicarbonate,[16] the unchanged quinone removed by filtration, and any turbidity in the

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[13] Schmidt and Spoun, *Ber.*, **55**, 1199 (1922).

[14] The oxidation of much larger units of 2-nitrophenanthraquinone was always attended by much lower percentage conversion.

[15] The direct use of recrystallized 2-nitrophenanthraquinone without reprecipitation from sulfuric acid invariably gave much lower yields.

[16] Some unoxidized quinone was always left in the crude product; the use of cold bicarbonate solutions for separation of the acid avoided its conversion to the corresponding diphenylene glycolic acid. The yield was based upon the unrecovered quinone, since the unoxidized material was very pure and was used for other runs.

resultant solution cleared up by boiling with Norite, and refiltering. The warm, clear, bright yellow filtrate was very slowly acidified with C. P. 50% sulfuric acid.[17]

Although all the papers[18] reporting this substance have involved oxidation of 2-nitrophenanthraquinone with potassium dichromate and sulfuric acid, the product has never been entirely pure and no yields have been given. Whereas Strasburger's pale yellow product melted at 217° and Schmidt and Spoun's "almost white" material fused at 214–216°, the acid obtained by our procedure in 92% yield was snow-white and melted sharply at 215.5–216.0° (220–221°, corr.); neutralization equivalent, 143.6; calcd., 143.5. No previous note of the unusually intense bitter taste of this acid appears in the literature.

**Conversion of 4-Nitrodiphenic Acid to 7-Nitrofluorenone-4-carboxylic Acid.**—4-Nitrodiphenic acid was heated at 155° ± 5° for ten minutes with 2.5 cc. of concd. sulfuric acid per gram of solid. After pouring the slightly cooled reaction product into water, the thick yellow precipitate was filtered from the boiling solution; yield, 100%; m. p. of crude product, 261–262°, uncorr., with decomposition. After recrystallization from glacial acetic acid, the pure yellow needles melted at 262.0–262.5° (269.0–269.5°, corr.), with decomposition. For analysis it was converted to the methyl ester.

METHYL ESTER.—Five and one-half g. of nitroketo acid was dissolved in 80 cc. of 95% methyl alcohol, the ice-cold solution saturated with dry hydrogen chloride, and refluxed for four hours. The crystalline product obtained on cooling was washed with sodium carbonate and twice recrystallized from benzene, giving bright yellow needles; m. p., 199.5–200.0° (203–204°, corr.).

*Anal.* Calcd. for $C_{15}H_9NO_5$: C, 63.60; H, 3.18; N, 4.95. Found: C, 63.27, 63.37; H, 3.30, 3.78; N, 5.21, 5.18.

OXIDATION.—Three and nine-tenths g. of nitroketo acid prepared from 4-nitrodiphenic acid was dissolved in potassium carbonate solution and boiled for two hours with 350 cc. of potassium permanganate per liter (0.01 g. of available oxygen per cc.). After decolorizing the excess of oxidant with methyl alcohol and filtering out the oxides of manganese, the alkaline filtrate was concentrated, acidified, and extracted with ether. On evaporation of this ether extract, clouds of nitrous fumes were evolved, indicating the presence of nitric acid. Oxidation of the ether residue was completed with concd. nitric acid and manganous nitrate, according to Bucher.[19] The white, crystalline acid obtained after recrystallization from water contained no nitrogen and gave an excellent fluorescein test on fusion with resorcinol and sulfuric acid. The sample melted at 190.5–191.0° (uncorr.); the recorded[20] value for hemimellitic acid is 190°. On heating above 200°, bubbles of gas came off and the reheated material melted at 194.5–195° (uncorr.). The recorded[20b] value for hemimellitic anhydride is 196°.

*Neut. equiv.* Subs., 0.0859, 0.0823: 10.94, 10.47 cc. of 0.1139 *N* NaOH. Calcd. for $C_9H_6O_6$ (hemimellitic acid): neut. equiv., 70.0. Found: 68.9, 69.0.

**Fluorenone-4-carboxylic Acid.**—The procedure of Graebe and Aubin,[21] carried out

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[17] 4-Nitrodiphenic acid has a strong tendency to form supersaturated solutions from which rapidly separating solid drags down any turbidity or discoloration. It is essential that crystal clear solutions be employed and that crystallization be induced by scratching from the first drop of excess of precipitating acid.

[18] (a) Strasburger, *Ber.*, **16**, 2347 (1883). (b) Schmidt and Austin, *Ber.*, **36**, 3732 (1903). (c) Mudrovcic, *Monatsh.*, **34**, 1441 (1913).

[19] Bucher, THIS JOURNAL, **32**, 220, 379 (1910).

[20] (a) "International Critical Tables," McGraw-Hill Book Co., New York, **1926**, vol. 1, p. 225. (b) Graebe and Leonhardt, *Ann.*, **290**, 221 (1896).

[21] Graebe and Aubin, *Ann.*, **247**, 275 (1888).

at 140° ± 5°, gave an 86% yield; m. p., 223–224° (uncorr.). Filtration of the finely divided, precipitated material was much hastened by the use of gravity filtration through filter cloth placed in a large Büchner funnel.

NITRATION.—Sixty-six and one-half g. of fluorenone-4-carboxylic acid was dissolved in 665 cc. of C. P. concd. nitric acid (d., 1.42) and the solution quickly brought to the boiling point. Reaction was self-sustaining at first but soon required application of heat; the flask was kept at the boiling point for just 45 minutes, and was shaken constantly after separation of the solid commenced. After pouring into 5 volumes of water the precipitate was filtered, washed free from nitric acid and dried at 105°; yield of crude nitration product, 62 g., or 76%. The very dense product was powdered and once recrystallized from 1550 cc. of glacial acetic acid. A loose compound of 7-nitrofluorenone-4-carboxylic acid with the solvent crystallized out and was filtered off; on washing with alcohol or water, or even on mere drying, the pale yellow addition product yielded brilliant yellow 7-nitrofluorenone-4-carboxylic acid; yield, 39 g., or 48%, and 63% of the crude mixed nitration product; m. p., 262.0–262.5° (uncorr.) By concentration of the mother liquor and repeated crystallization from 50% acetic acid, 5-nitrofluorenone-4-carboxylic acid was obtained; m. p., 232–233° (238–239°, corr.).

**Identification of Principal Nitration Product.**—Two g. of the nitration product melting at 262.0–262.5° was oxidized in the manner already described for the condensation product from 4-nitrodiphenic acid. The resultant white acid was dissolved in ammonium hydroxide, brought to neutrality and precipitated with silver nitrate solution. The flocculent white deposit was dried at 105° and analyzed for silver by ignition.

*Anal.* Calcd. for $C_9H_3Ag_3O_6$ (trisilver hemimellitate): Ag, 60.98. Found: 60.61, 60.66, 60.73.

In addition, mixed-melting-point determinations were carried out on the methyl esters of the nitroketo acids prepared by both methods, and on the acids themselves. No depression of the melting point of the mixtures was observed.

**Identification of the Secondary Nitration Product.**—A sample of 6-nitrodiphenic acid[22] was dissolved in 3 cc. of concd. sulfuric acid and kept at 155° for 15 minutes. After pouring into water, 0.9 g. (96% of the calculated amount) of 5-nitrofluorenone-4-carboxylic acid was obtained. One recrystallization from glacial acetic acid brought the yellow needles to a constant melting point of 232.5–233.5° (238–239°, corr.).

*Neut. equiv.* Subs., 0.1552: 4.12 cc. of 0.1027 *N* NaOH. Calcd. for $C_{14}H_7NO_5$: neut. equiv., 269.0. Found: 269.5.

The melting point of a mixture of the secondary nitration product with the above synthetic 5-nitrofluorenone-4-carboxylic acid showed no depression.

**7-Nitrofluorenone-4-carboxylic Acid Chloride.**—Fifteen and five-tenths g. of 7-nitrofluorenone-4-carboxylic acid was mixed with 12.8 g. of powdered phosphorus pentachloride and boiled for 30 minutes with 100 cc. of toluene. After removing the solvent and most of the phosphorus oxychloride by distillation in a moderate vacuum,[23] the solid was washed with benzene and filtered; yield, 16.1 g., or 98%. For most of our experiments this crude product was converted directly to amide, but recrystallization from anhydrous benzene yields the pure chloride in fine, yellow needles; m. p., 203.5–204.0° (207.5–208.0°, corr.). For analysis we found it essential to avoid hydrolysis by drying the product at room temperature in a vacuum desiccator over paraffin.

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[22] For this sample we are indebted to Mr. G. R. Tucker, who prepared it from 4-nitrophenanthraquinone according to the method described for 4-nitrodiphenic acid.

[23] We found later that distillation at ordinary pressure was entirely satisfactory, if care were taken not to superheat the residual solid.

*Anal.* Calcd. for $C_{14}H_6ClNO_4$: Cl, 12.35. Found (Carius): 12.34, 12.31, 12.32, 12.36.

**7-Nitrofluorenone-4-carboxylic Acid Amide.**—Fifteen g. of 7-nitrofluorenone-4-carboxylic acid chloride was suspended in 150 cc. of dry benzene and treated with a stream of dry ammonia gas for 20 minutes. The heavy, yellow precipitate was filtered, thoroughly dried, and agitated with water to remove ammonium salts; yield of final crude product, 14.0 g., or 100%.

For analysis, the crude product was recrystallized from glacial acetic acid to a constant melting point of 263.5–264.0° (270.5–271.0°, corr.). The substance crystallizes in bright yellow, microscopic needles which are insoluble in water, alcohol, chloroform, chlorobenzene, ether or *iso*-amyl acetate, but dissolve somewhat in hot *n*-butyl alcohol and more readily in hot acetic acid.

*Anal.* Calcd. for $C_{14}H_8N_2O_4$: C, 62.68; H, 2.98; N, 10.45. Found: C, 62.23, 62.38; H, 3.20, 3.20; N (Dumas), 10.59, 10.68.

**7-Nitro-4-aminofluorenone.**—Our procedure was to add to the finely powdered nitroketo-amide, a definite volume of solution whose potassium hypobromite and potassium hydroxide content were accurately known. The suspension was motor-stirred in an ice-bath for two to two and one-half hours, during which time the color changed from bright yellow to deep orange and a peculiar sweetish odor developed. After filtering off the separated by-product, a voluminous precipitate of the desired amine was obtained by heating the solution at the boiling point for half an hour. In one actual experiment, the hypobromite solution was prepared by bringing to 400 cc. the resultant mixture of separate solutions of 21.6 g. of potassium hydroxide and 12.8 g. of bromine in ice water. Of the standard mixture so prepared, 330 cc. was allowed to act on 16.1 g. of amide for two hours; yield, 5.1 g., or 35.4%.

The 7-nitro-4-aminofluorenone is insoluble in benzene, petroleum ether or carbon tetrachloride; it imparts a tinge of color to alcohol, acetone or ether; it is soluble in hot aniline, dimethylaniline, chlorobenzene, methylethyl ketone or pyridine. With 50% sulfuric acid or concd. hydrochloric acid it forms yellow salts which are soluble in an excess of warm acid but rapidly dissociate to the original amine on treatment with water. For analysis, a sample from sulfate was six times recrystallized from pyridine to a constant melting point of 284–285° (292–293°, corr.). The substance crystallizes in short, deep scarlet micro-needles.

*Anal.* Calcd. for $C_{13}H_8N_2O_3$: C, 65.00; H, 3.33; N, 11.66. Found: C, 65.03, 65.03; H, 3.58, 3.55; N, 11.73, 11.81.

**7-Nitro-4-acylaminofluorenone.**—Two and nine-tenths g. of amine was dissolved in a mixture of 15 g. of acetic acid and 30 g. of acetic anhydride. After boiling for a moment, a precipitate appeared with large evolution of heat. After ten minutes, the product was poured onto ice and after two recrystallizations from acetic acid containing 2% of acetic anhydride, was obtained in large, yellow spangles; m. p., 298–299° (307–308°, corr.).

In another experiment, 0.5 g. of amine and 4 cc. of acetic anhydride were dissolved in 8 cc. of pyridine and allowed to stand for two weeks at room temperature. After pouring into dil. sulfuric acid and twice recrystallizing from acetic acid the 96% yield so obtained, the product did not depress the melting point of a sample prepared by the first method.

*Anal.* Calcd. for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.57; N, 9.93. Found: C, 63.68, 63.77; H, 3.75, 3.67; N, 9.72.

The molecular weight of this acetyl derivative was determined by titration of the acetic acid produced on heating with an excess of 50% sulfuric acid for six hours.

*Mol. wt.* Subs., 0.1881: 6.45 cc. of 0.1029 *N* NaOH. Calcd. for $C_{15}H_{10}N_2O_4$: mol. wt., 282.1. Found: 283.4.

## 2. Nitration of Phenanthridone

**Phenanthridone.**—This was prepared substantially according to Graebe and Wander.[2] The crude product was purified by solution in alcoholic potassium hydroxide, followed by filtration and reprecipitation by dilution with water; yield, 83%; m. p., 284–285° (292–293°, corr.). Recrystallization of this product from acetic acid raised the melting point to Graebe's value of 285–286° (293–294°, corr.) and this was not changed by further treatment.

NITRATION.—Five g. of phenanthridone was dissolved in 62.5 cc. of C. P. concd. nitric acid (d., 1.42) by gentle warming. The solution suddenly began to turn red and almost instantly solidified with large evolution of heat. The cream-colored solid obtained on dilution with water amounted to 5.9 g., or 96% of the amount calculated for mononitrophenanthridone. Extraction of this crude substance with hot absolute alcohol gave, on evaporation of the solvent, 1.1 g. (19% of crude) of yellow solid; m. p., after recrystallization from acetic acid, 251–253° (257–259°, corr.). The residual white solid undissolved by alcohol was found to be so insoluble in acetic acid that it could not be recrystallized and its analysis was conducted on a sample which had merely been thoroughly extracted with the hot solvent. The melting point of a sample of sublimed material was found to be 368–370° (uncorr.) in a sealed capillary tube.

*Anal.* (yellow substance). Calcd. for $C_{13}H_8N_2O_3$: N, 11.67. Found: 11.54, 11.48.

*Anal.* (white substance). Calcd. for $C_{13}H_8N_2O_3$: N, 11.67. Found: 11.49, 11.83.

The melting point of a mixture of the yellow isomer with 7-nitrophenanthridone was depressed some 20°; that of a mixture of the white isomer with 2-nitrophenanthridone was depressed 40°.

## 3. Synthesis of 2-Nitro- and 7-Nitrophenanthridone through the Corresponding Nitrodiphenamic Acids

**4-Nitrodiphenic Anhydride.**—Twenty g. of 4-nitrodiphenic acid (m. p., 215–216°, uncorr.) was refluxed for four hours with 100 cc. of freshly distilled acetic anhydride. After concentrating to about 35 cc., 16.8 g. of the product melting at 206–207° (uncorr.) separated on cooling. This was filtered and washed with carbon tetrachloride; 1.5 g. of additional material was obtained on evaporating the mother liquor; total yield of 4-nitrodiphenic anhydride, 18.3 g., or 97%. By concentrating to a slightly less degree, absolutely pure anhydride, m. p. 207–207.5° (uncorr.), may be obtained in smaller yield, but we found the 206° product sufficiently pure for synthetic purposes. The substance may be crystallized from dry chlorobenzene but must be protected from moisture above room temperature in order to avoid rapid hydrolysis. We found that washing the product with cold sodium carbonate solution was unnecessary.

Pure 4-nitrodiphenic anhydride crystallizes in short, white needles; m. p., 207.0–207.5° (211.0–211.5°, corr.), without decomposition. The crystals are insoluble in petroleum ether, carbon disulfide and carbon tetrachloride.

*Anal.* Calcd. for $C_{14}H_7NO_5$: C, 62.43; H, 2.25; N, 5.21. Found: C, 62.53, 62.32; H, 2.94, 2.64; N, 5.45, 5.21.

As an additional check upon its identity the anhydride was hydrolyzed by alkali to the original 4-nitrodiphenic acid, which was identified by its failure to depress the melting point of a known sample.

**The Two Isomeric 4-Nitrodiphenamic Acids.**—To 21.0 g. of pure 4-nitrodiphenic anhydride, 84 cc. of ice-cold ammonium hydroxide (d., 0.90) was added in small increments, with constant shaking and cooling. Although the first portions of ammonium hydroxide appeared to dissolve the anhydride, the solid later increased in quantity. After standing in the cold for 30 minutes, 175 cc. of water dissolved the solid and the excess of ammonia in the filtered solution was neutralized with 75 cc. of glacial acetic acid. The mixture of nitrodiphenamic acids was then slowly precipitated with concd. hydrochloric acid as a dough-like mass which changed on standing for two hours to an easily filtered, crystalline solid. After washing with water and drying at 110° the product weighed 21.0 g.; yield, 94%; m. p., 164–173° (uncorr.).

**4-Nitro-2-diphenamic Acid** (XII).—The crude mixture was dissolved in 80 cc. of absolute alcohol, filtered hot, using 20 cc. of wash alcohol, and allowed to stand for two hours. The precipitated material was then recrystallized again from 60 cc. of alcohol, standing for two hours, as before. The precipitate of pure, high-melting isomer weighed 7.0 g.; yield, 32%; m. p., 199–200° (203–204°, corr.).

*Anal.* Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.72; H, 3.52; N, 9.72. Found: C, 58.82, 58.39; H, 3.87, 3.56; N, 10.16, 10.36.

The structure of this isomer follows from that of 2-nitrophenanthridone, which it yields on treatment with alkaline hypobromite.

**4-Nitro-2′-diphenamic Acid** (XIII).—The alcohol mother liquor, from the first crystallization of the crude mixture of nitrodiphenamic acids, was partially evaporated at ordinary temperature and the separating solid put through a long series of fractional crystallizations from alcohol, sometimes partially evaporating the solvent at room temperature and sometimes precipitating the solid with water. The acid crystallizes very sluggishly and frequently stands for a long time after scratching, before precipitation begins. Finally, 5.2 g. of white micro-needles, m. p. 162–163° (164–165°, corr.), was obtained; yield, 23%.

*Anal.* Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.72; H, 3.52; N, 9.72. Found: C, 59.02, 58.80; H, 3.64, 3.08; N, 10.23, 10.03.

The structure of this isomer follows from its synthesis from 4-nitrodiphenic anhydride and from that of 7-nitrophenanthridone, which it yields with alkaline hypobromite.

**2-Nitrophenanthridone** (XIV).—Three and eighty-four hundredths g. of high-melting 4-nitrodiphenamic acid was dissolved in an ice-cold solution of 7.53 g. of potassium hydroxide in 118 cc. of water. An alkaline hypobromite solution was prepared from 3.22 g. of bromine and 2.26 g. of potassium hydroxide in 83 cc. of ice water. These two solutions were mixed and motor-stirred in an ice-bath for 40 minutes, after which stirring was continued at 60–70° for half an hour. After cooling, the nitrophenanthridone was precipitated by saturation with sulfur dioxide. The solution was next made alkaline with sodium carbonate and the filtered precipitate dried at 110°; yield, 3.1 g., or 95%. After one recrystallization from acetic acid, the yellow needles melted in a sealed capillary tube at 348.5–349° (uncorr.), with decomposition.

*Anal.* Calcd. for $C_{13}H_8N_2O_3$: N, 11.67. Calcd. for $C_{13}H_{10}N_2O_4$ (intermediate amino acid): N, 10.86. Found: 11.94, 11.77.

OXIDATION TO *o*-PHTHALIC ACID.—One g. of the above nitrophenanthridone was dissolved in 5 cc. of concd. sulfuric acid and poured into 100 cc. of water. The mixture was made alkaline with 6 *N* sodium hydroxide solution; 6.0 g. of potassium permanganate (160% of the calculated amount) was added and the volume of solution brought up to 200 cc. After boiling for four hours, sulfur dioxide failed to produce any precipitate but decolorized the excess of oxidant. After being made alkaline during concentration to small volume, ether extraction of the acidified solution yielded a white solid; m. p., 160–168° (uncorr.). The aqueous layer gave a strong test for nitrate with diphenylamine reagent. After washing the white solid free from phthalonic acid with cold water, the melting point was 188–190° (191–192°, corr.), with evolution of gas. This value agrees with that recorded[24] for *o*-phthalic acid. The sample contained no nitrogen and gave a strong fluorescein test when heated with resorcinol and sulfuric acid. After fusion the sample remelted at 125–127° (126–128°, corr.); the recorded[25] value for *o*-phthalic anhydride is 130.8°. A sample of the acid was converted to *o*-phthalanil by heating with aniline according to Mulliken.[26] After two recrystallizations from alcohol the product melted at 204.5–205.5° (uncorr.) and failed to depress the melting point of a known sample prepared similarly from pure *o*-phthalic acid.

**7-Nitrophenanthridone (X).**—This isomer was prepared from the low-melting 4-nitrodiphenamic acid according to the procedure already described for 2-nitrophenanthridone. In an actual experiment, 2.288 g. of low-melting 4-nitrodiphenamic acid, with quantities of reagents proportional to those already cited, gave 1.56 g. of 7-nitrophenanthridone; yield, 81%. After two recrystallizations from glacial acetic acid, it was obtained in clusters of bright yellow, microcrystalline needles; m. p., 284–285° (292–293°, corr.).

*Anal.* Calcd. for $C_{13}H_8N_2O_3$: C, 64.97; H, 3.36; N, 11.67. Calcd. for $C_{13}H_{10}N_2O_4$, (intermediate amino acid): C, 60.44; H, 3.12; N, 10.86. Found: C, 64.95, 64.51; H, 3.96, 3.48; N, 11.81, 11.73.

## Summary

1. Both 2-nitro- and 7-nitrophenanthridone have been prepared from 4-nitrodiphenic anhydride, by way of two isomeric 4-nitrodiphenamic acids.

2. Direct nitration of phenanthridone was shown to give good yields of two other mononitrophenanthridones but none of the 2- or 7-nitro isomers.

3. Because of the instability of 7-nitrophenanthridone toward alkaline fusion, this isomer could not be so obtained from 7-nitro-4-aminofluorenone.

4. A simple procedure has been devised which gives excellent yields of *pure* 4-nitrodiphenic acid.

5. Ring closure of 4-nitrodiphenic acid with sulfuric acid was shown to occur in only one sense, yielding quantitatively 7-nitrofluorenone-4-carboxylic acid.

6. 7-Nitrofluorenone-4-carboxylic acid has also been prepared in excellent yield by direct nitration of fluorenone-4-carboxylic acid.

7. During the course of our study we have also prepared and characterized the following substances: 7-nitrofluorenone-4-carboxylic acid chloride, amide and methyl ester; 7-nitro-4-acylaminofluorenone.

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[24] Ref. 20 a, p. 216.

[25] Ref. 20 a, p. 215.

[26] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, **1904**, vol. 1, p. 85.