

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
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UNSYMMETRICAL PHENANTHRIDONES. II. A NEW
PREPARATIVE METHOD: 7-NITROPHENANTHRIDONE BY
BECKMANN REARRANGEMENT OF 2-NITROFLUORENONE
OXIME

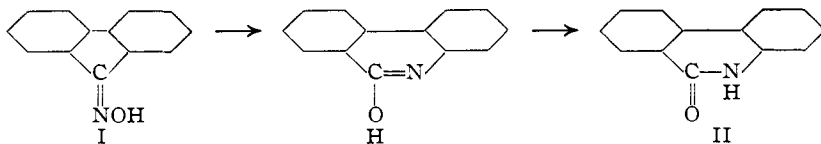
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Shortly after the discovery of the Beckmann rearrangement of oximes in 1884, Beckmann and Wegerhoff² attempted to expand the scope of the new reaction to the oximes of cyclic ketones. Studying fluorenone oxime as a typical example, they reported that heating with a mixture of acetic anhydride and hydrogen chloride in a closed tube effected only acetylation, and that the use of concentrated sulfuric acid as a rearranging agent yielded a mixture of sulfonic acids. After boiling the oxime with a solution of phosphorus pentachloride in phosphorus oxychloride, however, removal of the solvent left a viscous oil from which they were unable to isolate a chloride. Nevertheless, after treatment with water, the oil yielded a yellow powder from which a nearly colorless, chlorine-free compound melting at 287° was obtained. This material was formed in such small amount and proved so difficult to purify that after an analysis its definite characterization was abandoned.

Application of the usual principles of Beckmann rearrangement to the case of fluorenone oxime (I) indicates that the rearrangement product should have been phenanthridone (II).



At the time of Beckmann and Wegerhoff's work this substance was unknown, and although only four years later Graebe and Wander³ prepared the material by a method which demonstrated its structure, and their melting point of 293° was very close to that of Beckmann's product, no attempt to establish the identity of the two substances has ever been reported.

¹ This paper is constructed from a second portion of the 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 Beckmann and Wegerhoff, *Ann.*, **252**, 35 (1889).

³ Graebe and Wander, *Ann.*, **276**, 245 (1893).

That it is not unreasonable to expect Beckmann rearrangement of fluorenone oxime is indicated by the studies of Wallach⁴ who showed that cyclomethylene ketoximes were quite generally rearranged by concentrated sulfuric acid to isoximes or lactams of amino acids, into which they could readily be converted by hydrolysis. Thus, cyclopentanone oxime yielded the six-membered piperidone, otherwise known as the lactam of δ -aminovaleric acid. Again, Beckmann and Liesche,⁵ in an article which appeared during the progress of this research, have effected a normal rearrangement both of quinone monoxime and of anthraquinone monoxime. Except for Beckmann's early work, however, the only reference to the possible rearrangement of fluorenone oxime itself is the report of Pictet and Gonset⁶ who found that when heated with zinc chloride at 260–280°, a 30% yield of phenanthridone identical with Graebe and Wander's product could be isolated. Although the conditions used by Pictet and Gonset were far more vigorous than those of an ordinary Beckmann transformation, their results strengthened our belief that Beckmann and Wegerhoff's reaction product was really phenanthridone.

Our interest in this reaction was based upon the hope of using the Beckmann rearrangement of substituted fluorenone oximes as a method for the preparation of substituted phenanthridones. Not only is the literature of these substances very fragmentary but the synthesis of certain monosubstitution products from the corresponding diphenic acid derivatives is a process of considerable length and difficulty.⁷

We have repeated Beckmann and Wegerhoff's experiments on the rearrangement of fluorenone oxime by phosphorus pentachloride and by the method of mixed melting points established the identity of the product with phenanthridone synthesized according to Graebe and Wander.³ The change apparently involves nearly quantitative conversion of the oxime to a chloride which hydrolyzes slowly or rapidly, according to conditions, to give excellent yields of phenanthridone. Since our purpose was merely to establish the validity of the rearrangement, we have not attempted to study its mechanism in detail.

Although fluorenone oxime itself can exist in but one form, theory predicts for each of the unsymmetrical monosubstitution products the possible existence of two stereo-isomers, according to whether the substituted nucleus is on the same or opposite side of the carbon-nitrogen double bond as the oxime hydroxyl group. Beckmann rearrangement of these isomers would be expected to yield two different but isomeric

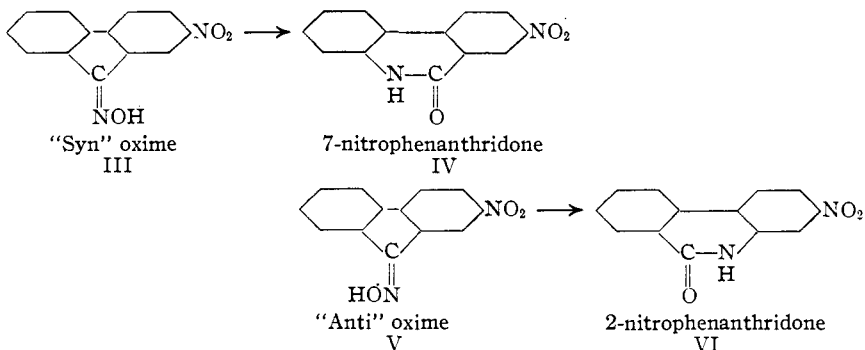
⁴ Wallach, *Ann.*, **309**, 1 (1899); *Ann.*, **312**, 171 (1900); *Ann.*, **346**, 249 (1906).

⁵ Beckmann and Liesche, *Ber.*, **56**, 1 (1923).

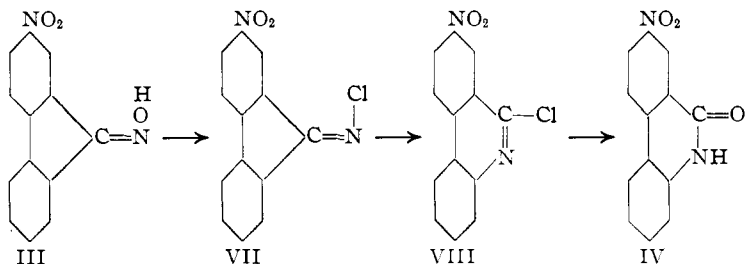
⁶ Pictet and Gonset, *Arch. sci. phys. nat.*, [4] **3**, 3751 (1897); *Chem. Centr.*, **1897**, I, 413.

⁷ Moore and Huntress, *THIS JOURNAL*, **49**, 1324 (1927).

substituted phenanthridones. Thus, assuming with Meisenheimer^{8,9,10} that *trans* interchange of radicals occurs, the expected products from the two forms of 2-nitrofluorenone oxime would be as follows



We have found, however, that treatment of 2-nitrofluorenone with hydroxylamine hydrochloride gives 75–85% yields of one of the two possible stereo-isomers, and that this product is rearranged by phosphorus pentachloride and oxychloride to give almost quantitative yields of 7-nitrophenanthridone. We have shown that the direct effect of the phosphorus halides is to replace chlorine for hydroxyl but that a mixture of two compounds is obtained which analyzes correctly for chlorine content yet is not readily separable by crystallization. Since reaction of this mixture with water yields 87% of 7-nitrophenanthridone with no indication of any of the 2-nitro isomer, we suspect that the mixture of chlorides represents an equilibrium between the oxime chloride and its rearrangement product, and that hydrolysis of the latter causes progressive conversion to the single 7-nitrophenanthridone as follows.



Whether this suspicion be confirmed or not, it is certain that oximation of 2-nitrofluorenone gives excellent yields of one stereo-isomer which undergoes smooth Beckmann transformation to give 7-nitrophenanthridone in yield of 90%. The process is therefore admirably suited to

⁸ Meisenheimer, *Ber.*, **54**, 3206 (1921).

⁹ Meisenheimer and Meis, *Ber.*, **57**, 289 (1924).

¹⁰ Meisenheimer, Zimmermann and Kummer, *Ann.*, **446**, 205 (1926).

serve as a method of preparation for this latter substance, which, it should be noted, is that isomer most difficult to obtain by the synthetic series involving the isomeric 4-nitrodiphenamic acids and recently reported by us.⁷ The new method possesses the very real advantage of starting from the easily obtainable fluorene¹¹ instead of from phenanthrene, and of requiring only a few stages as compared with the diphenic acid procedure. Should the studies now in progress in this Laboratory show that other position isomers and substituents likewise yield only one of two possible fluorenone oximes, the utility of this method as a synthetic tool in the further elucidation of phenanthridone chemistry will be much increased.

Experimental Part

Fluorenone.—This was prepared according to Graebe and Rateneau¹² by oxidation of fluorene with sodium dichromate in glacial acetic acid solution. The fluorene was purified by distillation from 10% of its weight of solid potassium hydroxide; yield of fluorenone, 92%.

Fluorenone Oxime (I).—We employed the procedure of Spiegler,¹³ heating 8.5 g. of pure fluorenone with 6.6 g. of hydroxylamine hydrochloride in 80 cc. of 70% alcohol for three hours. The yield was 82% of the theoretical and the melting point 192–193° (195–196° corr.).

Beckmann Rearrangement of Fluorenone Oxime to Phenanthridone.—Five g. (1 mole) of fluorenone oxime was boiled under reflux for five hours with 7.5 g. (1.4 mole) of phosphorus pentachloride dissolved in 50 cc. (21 moles) of phosphorus oxychloride. The oxime rapidly dissolved in the mixture, imparting to it a pale orange color and liberating much hydrogen chloride. On completion of the reaction the phosphorous oxychloride was removed by distillation at ordinary pressure and the residual yellowish-red viscous oil was worked with water. This treatment soon changed it to a yellow powder which weighed 5.0 g., melted at 282–289° (corr.) and contained chlorine. One-half of this powder was boiled with 100 cc. of 50% sulfuric acid for one and one-half hours. After pouring onto ice, 2.1 g. of nearly white solid separated which, like the original, also melted at 282–289° (corr.). After three recrystallizations from glacial acetic acid, using Norit decolorizing carbon in the first, the product was pure white, free from chlorine and melted at 285–286° (293–294° corr.).

Although the appearance and behavior of this material assured us that it was phenanthridone, we confirmed this by the method of mixed melting points using for comparison phenanthridone prepared from diphenic acid in a previous research.¹⁴ Samples of known pure phenanthridone, our rearrangement product and a mixture of equal weights of these two in capillary tubes attached to the same thermometer melted simultaneously at 285–286° (293–294° corr.). This value is that recorded by Graebe for phenanthridone and substantiates the identity of the rearrangement product.

2-Nitrofluorene.—This substance was prepared by nitration of fluorene according to Diels;¹⁵ yield of 2-nitro isomer, 66%; m. p. 154–154.5° (corr.).

2-Nitrofluorenone.—Continuing Diels' method, the 2-nitrofluorene so obtained

¹¹ This hydrocarbon is sold by the Eastman Kodak Company.

¹² Graebe and Rateneau, *Ann.*, **279**, 258 (1894).

¹³ Spiegler, *Monatsh.*, **5**, 195 (1884).

¹⁴ Ref. 7, p. 1332.

¹⁵ Diels, *Ber.*, **34**, 1758 (1901).

was dissolved in acetic acid and oxidized with sodium dichromate; yield, 91%; m. p. 214–216° (219–221° corr.).

2-Nitrofluorenone Oxime (III or V).—Six g. of pure 2-nitrofluorenone was suspended in 240 cc. of alcohol and boiled for one and one-half hours with 3.5 g. of hydroxylamine hydrochloride dissolved in the least possible volume of water. The ketone soon dissolved and a much paler yellow, curdy material began to separate. After cooling and filtering, the product was washed free from chloride with alcohol and dried at 110°; yield, 75%; m. p., with decomposition, 262.5–263 (269–270° corr.).

Repeated attempts to purify the crude product by recrystallization from benzene, alcohol, glacial acetic acid or *n*-butanol led to the discovery that the more times it was recrystallized, the lower and wider became the melting-point range. At the time this observation was regarded as highly disturbing but from the results of our later work it seems probable that the lowering of the melting point of the oxime was due to progressive rearrangement to the Beckmann product under the influence of temperature and solvent. We finally concluded that attempts at purification were futile and used directly for analysis the product obtained from carefully purified ketone and melting sharply at 262.5–263° (uncorr.) with vigorous decomposition.

Anal. Calcd. for $C_{13}H_9N_2O_3$: C, 64.97; H, 3.36; N, 11.68. Found: C, 64.69, 64.85; H, 3.40, 3.33; N, 12.21, 12.01.

HYDROLYSIS.—Saponification of the oxime with concentrated hydrochloric acid yielded a yellow solid, which was identified as 2-nitrofluorenone by mixed melting point, and a filtrate which gave on evaporation a solid which instantly reduced Tollens' reagent and gave Mulliken's¹⁶ color tests for hydroxylamine.

Beckmann Rearrangement of 2-Nitrofluorenone Oxime.—Twenty-three grams of 2-nitrofluorenone oxime was mixed with 34.5 g. of powdered phosphorus pentachloride and 200 cc. of phosphorus oxychloride and gently boiled under reflux for four hours. The liquid was divided into two equal portions and the solvent removed from each by distillation. The product from part A was allowed to crystallize, was then ground up in a mortar and allowed to stand in water for an hour. The residual lemon yellow solid was washed free from chloride and phosphate and after drying at 110° was found to melt at 153–173° and to contain chlorine. The residual solid from evaporation of part B was suspended in dry benzene for 39 hours; the benzene was then distilled off and the solid worked up with water as in part A. The product contained chlorine and melted at 152–193°.

Examination of Chlorine Compound from Part A.—A sample of the 153–173° product from part A was extracted with benzene, yielding a yellow solid melting at 150–185°. To remove possible nitrophenanthridone produced by hydrolysis we soaked the solid in strong alcoholic potassium hydroxide solution for a few minutes but failed to note the red color which accompanies the solution of 7-nitrophenanthridone under such circumstances. The washed solid was pale greenish-white in color and melted over the same range as before. It was analyzed for chlorine by the Carius method.

Anal. Calcd. for $C_{13}H_7ClN_2O_2$: Cl, 13.72; for $C_{13}H_7Cl_2NO_2$: 25.38. Found: Cl, 12.88, 13.09.

¹⁶ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1916, Vol. II, p. 30.

A sample of the product from part B was extracted with benzene in the same way and the product obtained was twice again recrystallized from benzene dried over sodium wire. The product melted at 155–170°. No alcoholic alkali treatment was employed. After drying at 50° in a vacuum the sample was analyzed for chlorine by the Carius method as before.

Anal. Calcd. for $C_{13}H_7ClN_2O_2$: Cl, 13.72; for $C_{13}H_7Cl_2NO_2$: 25.38. Found: Cl, 12.90, 13.00, 12.83, 12.99.

These data indicate that the materials from parts A and B are undoubtedly identical and that the chlorine content of samples purified by entirely different methods corresponds fairly well either to 2-nitrofluorenone-9-iminochloride (VII) or its rearrangement product 7-nitro-9-mesochlorophenanthridine (VIII) but not at all to 2-nitro-9,9-dichlorofluorene. The broad fusion range and its failure to change on repeated recrystallization suggest that we have an equilibrium mixture of the oxime chloride and its rearrangement product.

Conversion of Chlorine Compounds into 7-Nitrophenanthridone

Use of Chlorobenzene.—With the idea that a solvent more closely related to the substance might facilitate isomerization of one chloride to the other, 3 g. of crude chloride was boiled with 50 cc. of chlorobenzene. Nearly all of the solid dissolved and, after filtering and cooling, 0.50 g. of yellow solid giving only a slight test for chlorine and melting at 270–274° was deposited. This was purified by recrystallization from acetic acid, reprecipitation by sulfur dioxide from alcoholic potassium hydroxide solution and four subsequent crystallizations from acetic acid. The melting point of the yellow, chlorine-free substance was now 282–284° (uncorr.) and a mixture of it with known 7-nitrophenanthridone melted at the same temperature.

Use of Acetic Acid.—On the hypothesis that the production of 7-nitrophenanthridone from the chloride mixture would be facilitated by the presence of water in a mutual solvent, a sample of crude chloride melting at 150–170° was boiled with strong acetic acid for an hour. Hydrogen chloride was evolved and the solid obtained on cooling was free from halogen and melted at 285–292°. After purification from alcoholic alkali in the usual way, a bright yellow sample resulted, melting at 286–289° (uncorr.) and subliming in short, yellow needles like 7-nitrophenanthridone. The melting point of a sample of the latter was not depressed by admixture with the rearrangement product.

Use of 50% Sulfuric Acid.—With the original intention of hydrolyzing the oxime chloride to 2-nitrofluorenone, a sample of crude chloride was boiled with 50% c. p. sulfuric acid for over an hour. Hydrogen chloride was evolved as before, and upon dilution a yellow solid melting at 275–280° and free from halogen was obtained. Three recrystallizations from acetic acid raised the melting point to 284–285° (292–293° corr.). The melting point of its mixture with known 7-nitrophenanthridone melting at 284–285° (uncorr.) was the same.

Semiquantitative Study of Oxime Rearrangement.—Three g. of 2-nitrofluorenone oxime was refluxed for six hours with 4.5 g. of phosphorus pentachloride and 25 cc. of phosphorus oxychloride. The crude chlorine material obtained in the usual way melted at 150–170° (uncorr.) and weighed 3.11 g., corresponding to 96% of the theoretical. On boiling with 100 cc. of 50% sulfuric acid for one and one-half hours, dilution yielded 2.7 g. of crude product corresponding to 95% conversion of the chloride. After reprecipitation from alcoholic alkali it melted at 282–284° (290–292° corr.).

Anal. This was carried out on the rearrangement product melting at 284–285° (uncorr.). Calcd. for $C_{13}H_9N_2O_3$: C, 64.97; H, 3.36; N, 11.67. Found: C, 64.59, 64.51; H, 3.80, 3.89; N, 11.99, 11.99.

Summary

1. Fluorenone oxime has been shown to undergo a normal Beckmann rearrangement, yielding phenanthridone.
2. Oximation of 2-nitrofluorenone has been shown to yield mainly, if not entirely, one of two possible stereo-isomers.
3. Beckmann rearrangement of this 2-nitrofluorenone oxime to 7-nitrophenanthridone has been effected in yields of 90% and the method shown to be of preparative significance.

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THE REARRANGEMENT OF ISOPROPYLETHYLENE TO TRIMETHYLETHYLENE AND THE PYROGENIC DECOMPOSITION OF PENTENE-2 AND TRIMETHYLETHYLENE

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One of the major subjects under investigation in this Laboratory is the influence of structure on the reactivity of atoms and groups in organic compounds. The problem is being studied from two points of view; in one the rates at which the members of a series of analogous compounds react with a fixed substance is being studied;² in the other the conditions are being investigated under which certain molecular rearrangements take place and under which definite bonds are severed through the influence of heat and catalytic agents. This paper contains the preliminary results obtained in the study of three amylenes from the second point of view.

A detailed study of the properties of the amylenes is of particular interest on account of the fact that certain of these hydrocarbons are formed in the cracking of petroleum and are now of importance as sources from which amyl alcohols are prepared on a large scale.

The amylenes selected for study were pentene-2, trimethylethylene, and *isopropylethylene*. These compounds can be prepared readily from easily available substances and possess structures that make possible the study of the effect of the position of the double bond on rearrangements and the severing of the molecules under the influence of heat. In *isopropylethylene* the double bond is in position 1, in pentene-2 in position

¹ From the thesis presented by Raymond Reuter in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1925. Grasselli Scholar in Chemistry 1924-1925.

² Norris and Ashdown, *THIS JOURNAL*, **47**, 837 (1925).