THE REACTION OF 2-BROMO-2-NITRO-1,3-INDANDIONE WITH PYRIDINE

METRO

THE REACTION OF 2-BROMO-2-NITRO-1,3-INDANDIONE WITH PYRIDINE

A Thesis

by

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GENERAL INTRODUCTION

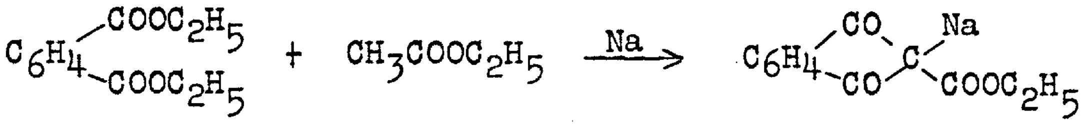
The main object of this work was to investigate the reaction of 2-bromo-2-nitro-1,3-indandione with pyridine in order to elucidate the chemical character of the former compound and of the bromine atom in particular. From the previous publications of other workers it is known that the bromine atom is very active in 2-bromo-2-nitro-1,3-indandione; therefore two possibilities could be foreseen in the interaction of the above named substances: first, the formation of a pyridinium salt with bromine as an anion, and second, the action of 2-bromo-2-nitro-1,3-indandione as a brominating and an oxidizing agent on pyridine.

The other problem in this research was to study the interaction of pyridine perbromide with aniline and some other amines.

HISTORICAL INTRODUCTION

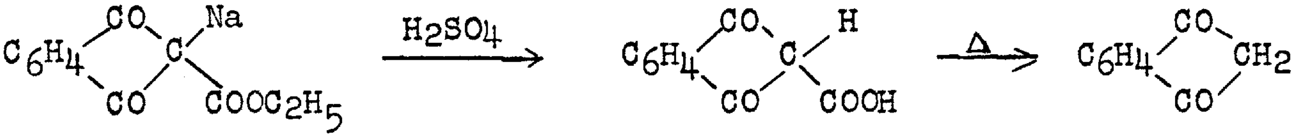
Synthesis and Structure of 2-Nitro-1,3-indandione and 2-Bromo-2-nitro-1,3-indandione

In 1888 Wislicenus prepared 1,3-indandione(1,3-diketohydrindene) by means of an ester condensation (1,2). He treated ethyl phthalate and ethyl acetate with sodium wire or sodium ethoxide from which the stable, yellow salt 2-sodio-2-carbethoxy-1,3-indandione I was obtained.



I

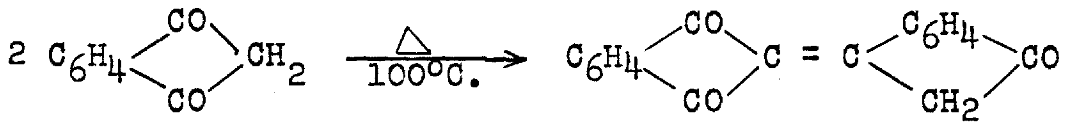
The sodium salt of 2-carbethoxy-1,3-indandione I was readily transformed into the desired product, 1,3-indandione III by decarboxylation with dilute sulfuric acid, maintaining careful temperature control. The intermediate product, 2-carboxy-1,3-indandione II was not isolated; because of its great instability it immediately underwent decarboxylation.



I II III

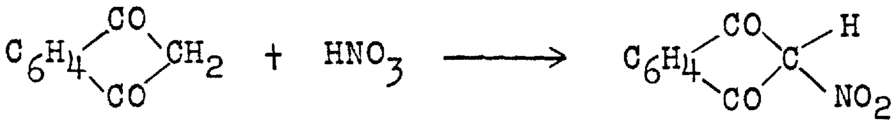
1,3-Indandione III was a white or pale yellow microcrystalline powder which melted at 129-131°C. The yield was reported as almost quantitative.

α,γ-Diketohydrindene(1,3-indandione) was a fairly unstable material. If it were heated without a solvent or with water around 100°C. in the presence of acids or bases, a molecule of water was split out from two molecules of indandione to form bindone IV. Bindone (anhydro-bisindandione) was a quite stable substance; it formed a characteristic dark blue solution when added to a solution of aniline in acetic acid. Bindone was a light tan colored solid which melted around 200°C.



III IV

Wanag nitrated 1,3-indandione III with fuming nitric acid, (3). He dissolved the 1,3-indandione in glacial acetic acid and added fuming nitric acid which had been diluted with glacial acetic acid. On cooling the mixture, he obtained a beautiful yellow crystalline compound which melted at 113-114°C. with decomposition. The yield was 78% of the theoretical.



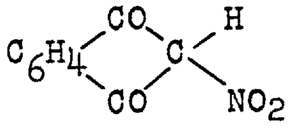
III V

In order to show that the nitro group was on the four membered ring and not on the benzene nucleus, Wanag (3) attempted to cleave the 2-nitro-1,3-indandione V into the expected phthalic acid and nitromethane. He observed that dilute acids and bases had no effect on 2-nitro-1,3-indandione V; concentrated sodium hydroxide caused an evolution of ammonia gas. This unexpected result found an explanation in the fact that the nitromethane was broken down into carbon dioxide and ammonia. If during the nitration, the nitro group had entered the benzene nucleus, the hydrolysis product should have been nitro-phthalic acid instead of phthalic acid which was isolated.

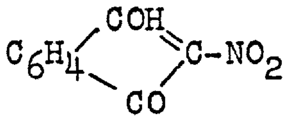
Aqueous solutions of 2-nitro-1,3-indandione V were acidic and could be titrated with bases. Stable salts were formed by many organic bases and this finding of Wanag has proved valuable for the isolation and identification for a great number of amines and other organic bases (4,5). An extensive list of 2-nitro-1,3-indandione salts has been published by Christensen, Wang, Davies and Harris (6), which should prove quite useful for identifying organic bases. Rosenthaler (7) used 2-nitro-1,3-indandione to study the crystal structure of alkaloids; he gave no melting points or analytical data. Müller (8) extended the use of this reagent for the identification of some miscellaneous compounds, i.e., arginine, cadaverine, methyl guanidine, creatinine, histidine, histamine and glycine.

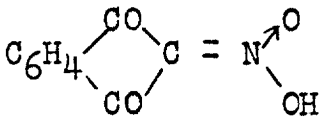
Salts of 2-nitro-1,3-indandione were formed by many metals such as silver, lead, and monovalent mercury; these salts were insoluble in water. A deep violet salt was formed with ferrous ion, which crystallized out as violet hexagonal crystals with four molecules of water of crystallization; Wanag (3) suggested that this salt could be used for the detection of iron. The salts of sodium, potassium and ammonia were reported as being sensitive to light. Many other salts were prepared such as barium, strontium, calcium, magnesium and trivalent iron.

Concentrated acids like hydrochloric precipitated 2-nitro-1,3-indandione V from aqueous solutions in the form of bright yellow crystals. 2-Nitro-1,3-indandione V formed both chloro VII and bromo VI derivatives but it could not be acetylated or benzoylated; therefore Wanag and Bungs (9) assumed that in solution the nitro-ketone did not exist Instead there was the nitro-enol or the aci- form (nitronic acid).



V

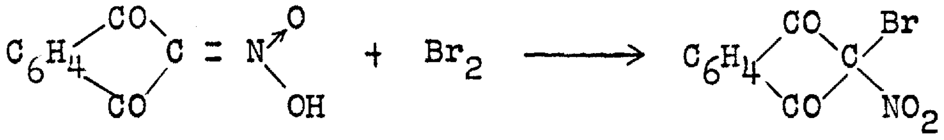




The above-mentioned workers attempted to determine the ratio of keto to enol by the K.H. Meyer titration method (10). Various solutions of V were prepared and each solution was treated with a solution of bromine in the same solvent until an excess was present; five more drops of bromine solution was added and the time was noted for the excess to disappear (formation of 2-bromo-2-nitro-1,3-indandione VI). The percentages of enol or aci- forms in the various solvents were reported as follows: benzene, 10%; ether, 38%; acetic acid, 88%; ethyl alcohol, 90%; and water, 98%. From these data Wanag and Bungs (9) concluded that 2-nitro-1,3-indandione V existed in solution as the nitronic acid. Wanag and Gudrinieze (11) observed that an aqueous solution of 2-nitro-1,3-indandione V gave no color test when ferric chloride solution was added.

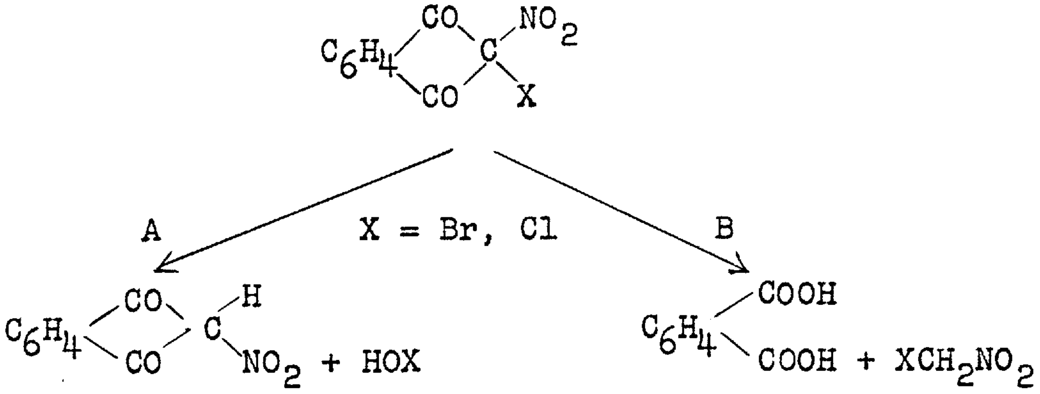
Using essentially the same procedure as in the above titration Wanag (3) prepared 2-bromo-2-nitro-1,3-

indandione VI by dissolving the 2-nitro-1,3-indandione V in water and then adding an excess of bromine water. The product, 2-bromo-2-nitro-1,3-indandione VI, was a white crystalline solid which was unstable in moist air and turned yellow because of the reformed 2-nitro-1,3-indandione V. No yield was given in the initial publication but a 98% yield was claimed in a later communication by Wanag and Lode (12).



V VI

Some studies were done on 2-chloro-2-nitro-1,3-indandione VII and 2-bromo-2-nitro-1,3-indandione VI toward various hydrolytic agents such as sulfuric acid, sodium hydroxide and water by Wanag and Bungs (13). 2-Bromo-2-nitro-1,3-indandione VI, when allowed to react with water, gave hypobromous acid and 2-nitro-1,3-indandione V, while under the same conditions 2-chloro-2-nitro-1,3-indandione VII was hydrolyzed to phthalic acid and chloronitromethane. When the same reaction was studied at a higher temperature the same products were formed, but much faster. In a minute VII gave phthalic acid and chloronitromethane; VI yielded 2-nitro-1,3-indandione and phthalic acid. Dilute sulfuric acid hydrolyzed both VI and VII very easily into phthalic acid and bromonitromethane or phthalic acid and chloronitromethane. With 0.2 N sodium hydroxide solution the behavior resembled the action of water; VI was cleaved into 2-nitro-1,3-indandione and VII into phthalic acid. From these examples it appeared that the 2-halo-2-nitro-1,3-indandiones reacted with these reagents in a definite fashion.



2-Chloro-2-nitro-1,3-indandione VII always followed the B route while 2-bromo-2-nitro-1,3-indandione VI followed either A or B, depending on the conditions.

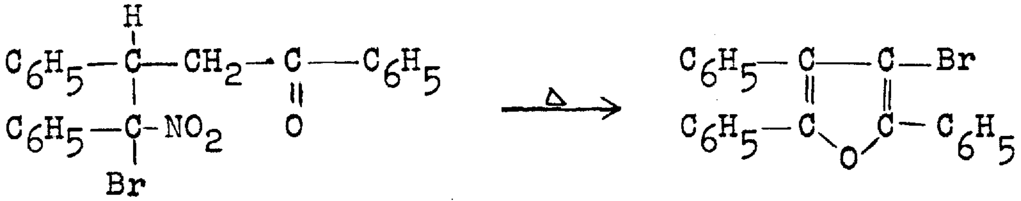
The halogen derivatives of 2-nitro-1,3-indandione V showed a characteristic behavior toward sodium iodide in that they oxidized the iodide to free iodine; this reaction was also given by alpha bromoketones. In an aqueous solution the reaction between sodium iodide and 2-bromo-2-nitro-1,3-indandione VI was much faster than the reaction between 2-chloro-2-nitro-1,3-indandione VII. Flatow (14) investigated the ease of removal of halogen from 2-chloro-2-carbethoxy-1,3-indandione and 2-bromo-2-carbethoxy-1,3-indandione and because the bromine was removed at a faster rate, he concluded the two compounds had different structures. Ziegler (15) showed full structural similarity for N-chloro-phthalimide and N-bromo-phthalimide. These two compounds were similar to the indandione derivatives; the N-halo-phthalimides showed great differences in the rate of halogen removal. N-Bromo-phthalimide was found to be a good brominating agent; the N-chloro-phthalimide hardly reacted under the same conditions. Still another comparison could be drawn, e.g., the differences in reactivity of bromo-succinimide as compared to chloro-succinimide. There was therefore no basis for Flatow's conclusion. Furthermore, the color of the 2-halo-2-nitro-1,3-indandiones was additional evidence for their structures, because both 2-bromo-2-nitro-1,3-indandione VI and 2-chloro-2-nitro-1,3-indandione VII were colorless in the solid form as well as in solution. Hantzsch (16) had shown that indandione derivatives were colorless in contrast to the hydroxyindones which possessed a deep yellow or orange color. It was assumed that both VI and VII were derivatives of indandione.

Wanag (3) reported that 2-bromo-2-nitro-1,3-indandione VI formed a solid product with pyridine and nothing further was said concerning the nature of the product. He also mentioned that VI acted as a brominating agent on some organic compounds, but no examples were given.

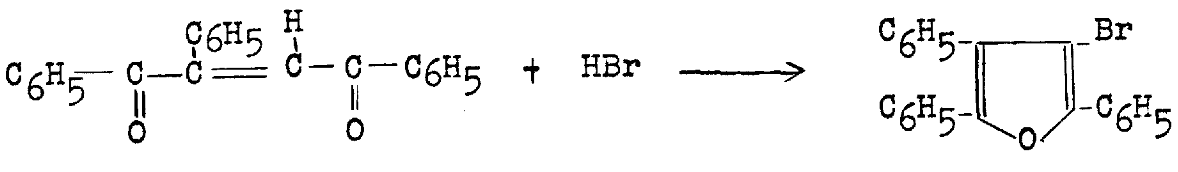
A literature survey revealed that only a limited amount of work was performed on bromo-nitro compounds. The previous investigations were pyrolytic studies. Some examples have been included in this section to complete the historical background on these unusual compounds.

The Chemistry of Bromo-nitro Compounds

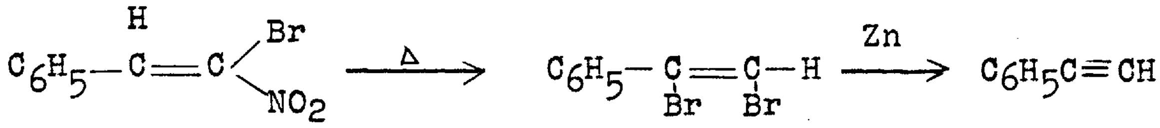
When γ-bromo-γ-nitro-β,γ-diphenyl butyrophenone was heated above its melting point, gas was evolved, and a chemically inert substance remained to which Allen and Rosener (17) assigned a furan structure. The correctness of this assumption was shown by the following reactions.



A synthesis of the 2,3,5-triphenyl-4-bromo furan was accomplished by reacting α,β-dibenzoylstyrene with hydrogen bromide.



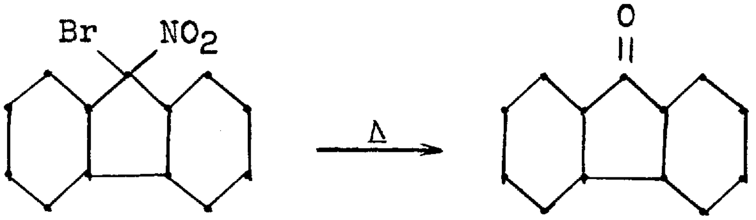
β-Bromo-β-nitro styrene was then subjected to pyrolysis by Allen and here again gases were evolved when the compound was heated above its melting point. This reaction was not as clear cut as Allen's first example because considerable carbonaceous matter was formed. The principal reaction product was α, β-dibromo styrene; some benzoic acid was also isolated.



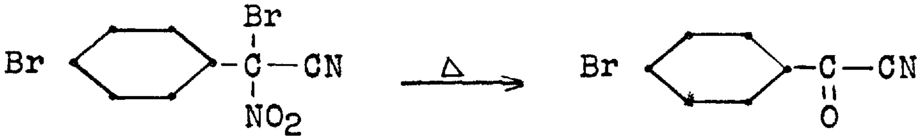
The structure of the dibromide was verified by treating it with zinc which gave the known phenylacetylene.

β-Bromo-β-nitro-α,α-diphenyl ethylene was also subjected to pyrolysis by Allen. The main reaction product was β, β-dibromo-α,α-diphenyl ethylene.

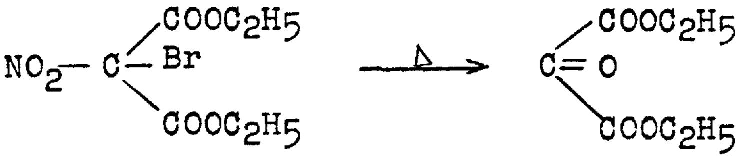
Wislicenus and Waldmüller (18) had previously studied the pyrolysis of 9-bromo-9-nitro-fluorene which by this treatment was transformed into fluorenone.



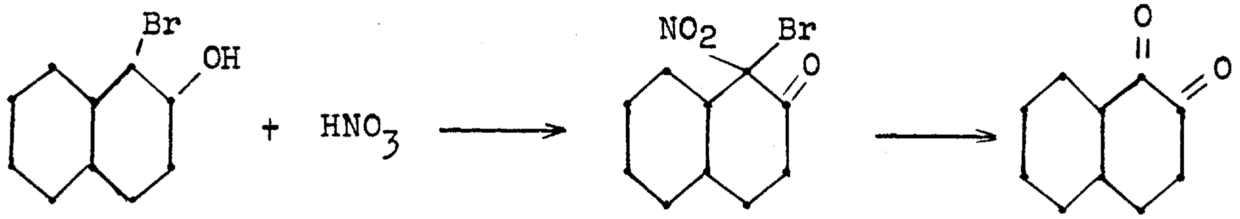
The pyrolysis of 4-bromophenyl-nitro-bromo-cyanomethane by Wislicenus and Elvert (19) followed in a similar fashion.



Willstätter and Hottenroth (20) obtained oxo-malonic ester by heating bromo-nitro-malonic ester above its melting point.



Fries and Roth (21) had shown that ortho quinones were obtained from the pyrolysis of polynuclear ortho-bromo, ortho-nitro ketones.



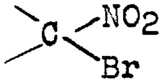
Many liquid halonitro compounds also decomposed on distillation but these have not been thoroughly investigated. A careful study by Gardner and Fox (22) on chloropicrin showed that phosgene was the main reaction product.

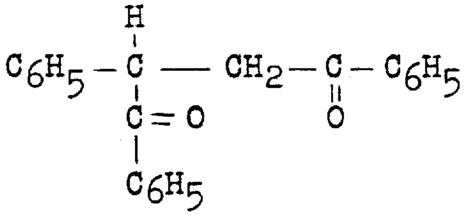
$$Cl_3C-NO_2 \longrightarrow COCl_2 + NOCl$$

The nitrosyl chloride was collected in sulfuric acid;

$$NOCl + H_2SO_4 \longrightarrow HCl + SO_2 \cdot OH \cdot ONO$$

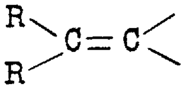
the solution had all the properties of nitrosylsulfuric. It was not possible to separate completely the sulfuric acid from the nitrosylsulfuric acid. Some white crystals were obtained by distillation of the mixture which melted around 30°C. They dissolved in water and formed a mixture of sulfuric and nitric acids. The nitrosyl chloride was determined by analyzing the amount of sulfuric acid obtained from the hydrolysis of the nitrosylsulfuric acid.

The net result in nearly all cases was the replacement of  by $>C=O$ but this conclusion did not apply in all instances. It seemed that the formation of the substituted furan in the first example was of an entirely different nature and the product should have been desylacetophenone.

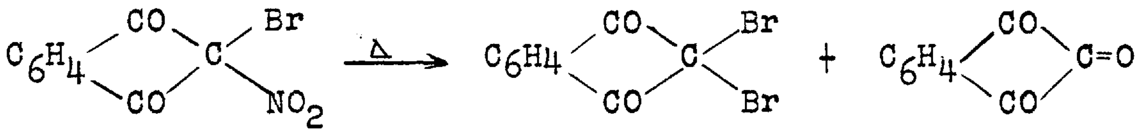


$$C_6H_5-\underset{\underset{\displaystyle C_6H_5}{|}}{\underset{C=O}{\overset{H}{C}}}-CH_2-\underset{O}{\overset{}{C}}-C_6H_5$$

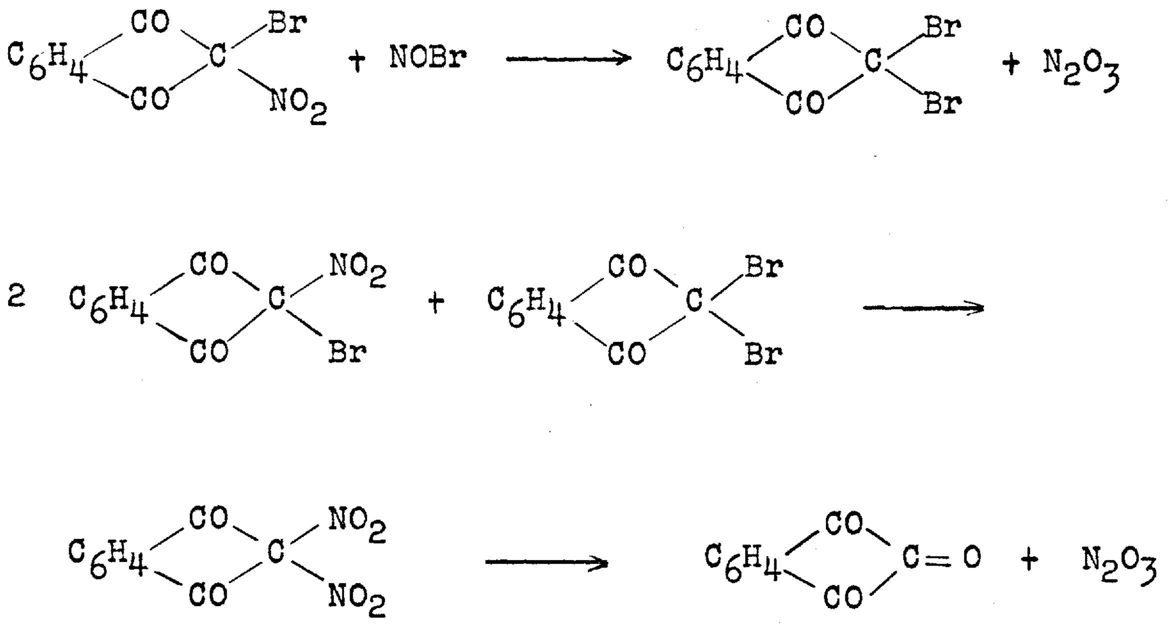
As a matter of fact when desylacetophenone was brominated the product was 2,3,5-triphenyl-4-bromofuran. This reaction was observed by Allen and Hermann (23) and showed that bromofuran would be expected if the intermediate were the keto compound and it was assumed that the reaction went by this path.

The ethylenic compounds were in a somewhat different category; the products should have been ketenes which were never obtained. However, the decompositions were never quantitative! If one assumed that a transitory diradical was formed during the pyrolysis it was then easy to account for the products in a more satisfactory manner because the diradical  could combine with bromine or oxygen to yield the dibromide or diphenyl ketene. If this mechanism were applied to 9-bromo-9-nitro-fluorene the expected product would have been 9,9-dibromofluorene; instead, the product was fluorenone. When 9-nitrofluorene was pyrolyzed the product was fluorenone, which seemed to indicate that oxidation rather than bromination occurred with saturated bromonitro compounds.

The investigation of Wanag and Lode (12) proved to be very interesting; they studied the pyrolysis of 2-bromo-2-nitro-1,3-indandione. In this particular case both possible products were isolated, i.e. 2,2-dibromo-1,3-indandione and ninhydrin.



The dibromide was obtained in a greater yield; they gave the following reactions to account for the reaction products. The 2,2-dinitro-1,3-indandione was not isolated as a reaction product but it was considered as the predecessor of the ninhydrin.

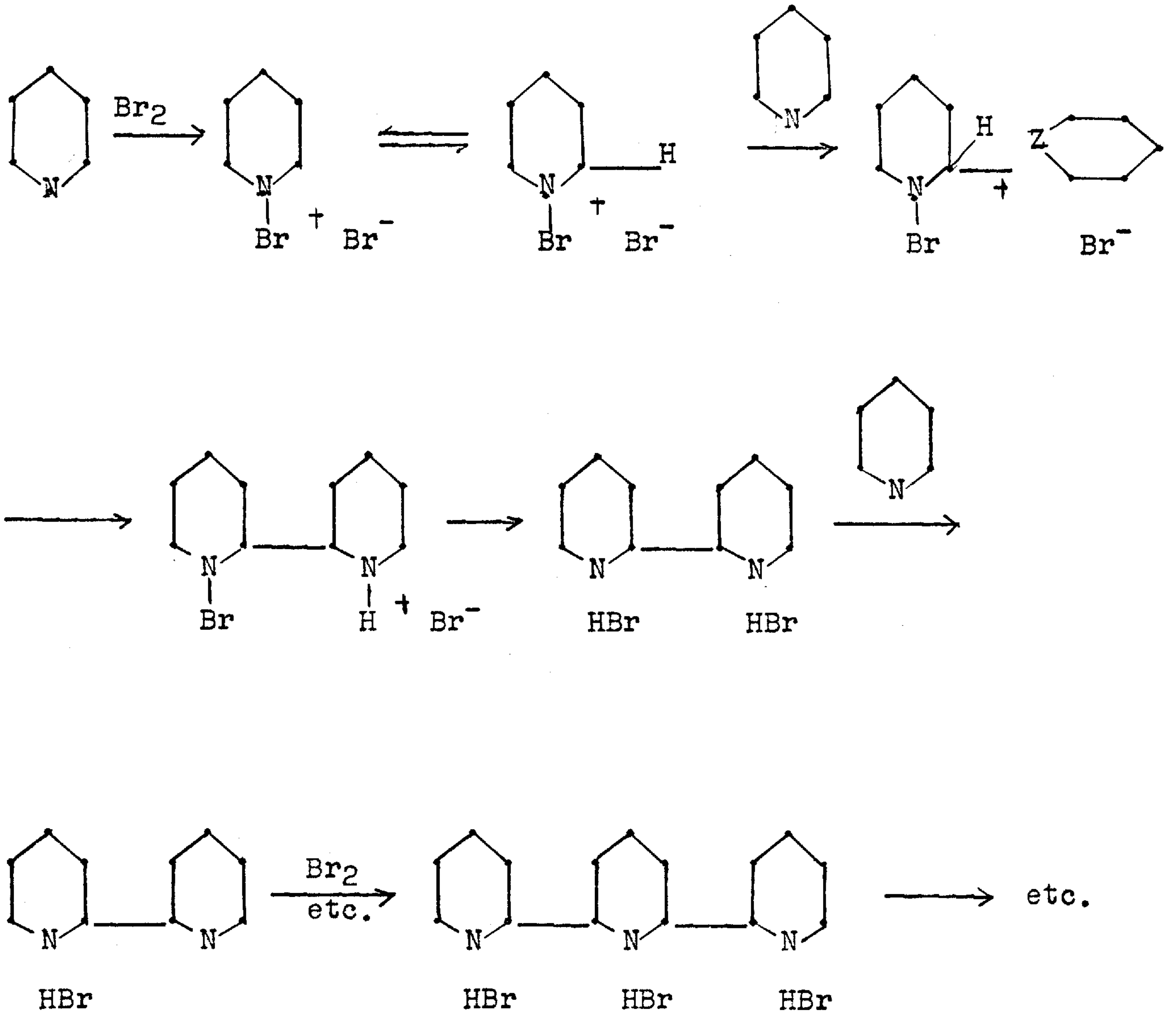


Allen and Wilson (24) suggested that the formation of the keto products occurred by an oxidative mechanism while the dibromides formed through a diradical intermediate.

The Reaction of Pyridine with Bromine

The bromination of pyridine was usually accomplished by a vapor phase process according to Wibaut and Hertog (25) which involved the reaction of bromine with pyridine at 300°C. The two reactants were passed through a tube maintained at that temperature. The product of the vapor phase process was a mixture of 3-bromo-pyridine and 3,5-dibromo-pyridine. When the temperature was raised to 500°C., 2-bromo-pyridine was the principal product according to McElvain and Goese (26).

They also tried to brominate pyridine by the use of liquid bromine; the product was an orange colored pyridine perbromide. This pyridine perbromide, when heated to around 250°C., underwent auto-bromination to give brominated pyridines. About one half of the pyridine was converted to a black tar which was also the main product from the vapor phase reaction. The black tar as it was formed in the reaction was a hydrobromide which was quite soluble in water; the free base which was obtained by treating the tar with alkali contained no halogen and had no melting point. An elementary analysis gave the following values: carbon 75%, hydrogen 5.2% and nitrogen 17%. The tar gave a deep red solution with alcohol and from these facts McElvain assigned a polypyridyl structure. The linkages were not necessarily through the alpha positions and could have been represented as joined through the gamma positions.



Widely varying data were obtained concerning the composition of the perbromides of pyridine. Anderson (27) assigned C_5H_5NBr to the compound which he obtained by treating pyridine with bromine in an aqueous solution. Grimaux (28) allowed pyridine to react with three times its volume of bromine; he obtained a red crystalline, unstable compound which melted at 126°C; he assigned the formula $(C_5H_5NBr_2)_2HBr$ to his product. Trowbridge and Diehl (29) were unable to obtain a definite compound by allowing bromine to react with an aqueous solution of pyridine. By using chloroform as a solvent they obtained a dark red crystalline compound which melted at 58.5°C. and analyzed for $C_5H_5NBr_4$. This compound was unstable and on standing lost bromine with the subsequent formation of $C_5H_5NBr_2$, m.p. 94-95°C.

Trowbridge and Diehl in the same communication obtained a very stable orange compound which melted at 125°C. This compound was prepared by aspirating bromine through a water solution of pyridine hydrobromide until the original crystals dissolved in the excess of bromine. They assigned the following formula to the product, $(C_5H_5NHBr)_2Br_3$. This may have been the same compound which was isolated by Grimaux; however, Trowbridge and Diehl's compound was stable even when heated on a water bath, while Grimaux's product was very unstable. Also reported by Trowbridge and Diehl (29) was a compound $C_5H_5N \cdot HBr \cdot Br$ which they obtained by allowing pyridine hydrobromide to react with bromine in chloroform. By allowing bromine to react with an aqueous solution of pyridine hydrobromide they obtained two products, (a) containing 41.95% bromine which was a mixture of $C_5H_5N \cdot HBr \cdot Br_2$ and $C_5H_5N \cdot HBr \cdot Br$ and (b) containing 33.66% bromine which was assumed to be $C_5H_5NHBr.Br$, m.p. 93°C.

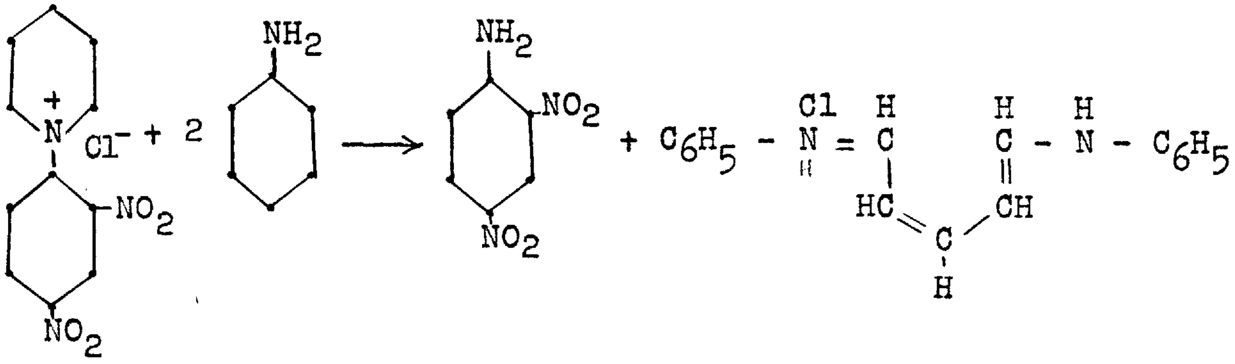
Hoffman (30) allowed pyridine hydrochloride to react with bromine; the product was an orange-yellow crystalline substance. He did not analyze the compound, however, he suggested the material was pyridine perbromide $C_5H_5N \cdot Br_2$.

McElvain and Englert (31) improved the above method for the preparation of the pyridine hydrobromide perbromides of Trowbridge and Diehl. They used glacial acetic acid as the solvent for the reaction. By using equimolar amounts of bromine and pyridine hydrobromide they obtained a product which analyzed for $C_5H_5NHBr \cdot Br_2$, m.p. 132-134°C. By using a 2:1 ratio of pyridine hydrobromide to bromine, a product was obtained which was probably $C_5H_5N \cdot HBr \cdot Br$, m.p. 101-103°C. The product which melted at 132-134°C., when heated to reflux temperature, gave a 40% yield of 3,5-dibromo-pyridine. The lower melting product under the same treatment yielded 36% 3-bromo-pyridine and 36% 3,5-dibromo-pyridine.

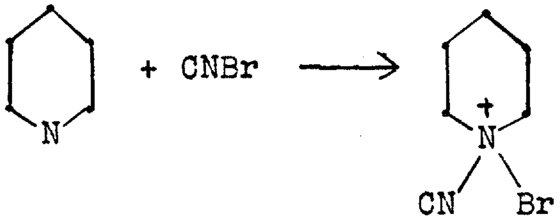
Williams (32) prepared pyridine perhalides by slowly adding the calculated volume of halogen in carbon tetrachloride to the calculated volume of pyridine in the same solvent. Using bromine he prepared pyridine perbromide $C_5H_5NBr_2$ which was an orange-red crystalline compound. This perbromide decomposed on standing; it could not be recrystallized, m.p. 62-63°C.

The Ring Opening of Pyridine

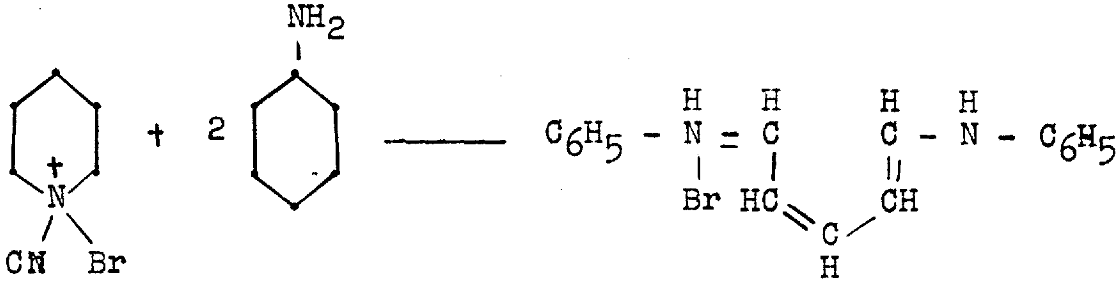
Zincke and his co-workers demonstrated that the pyridine ring of 2,4-dinitro-pyridinium chloride could be ruptured in a remarkable manner giving rise to 2,4-dinitro aniline and glutacondialdehyde (33,34,35). The five carbon aldehyde which was produced was very unstable and was not isolated; its formation was inferred by the preparation of its dianil.



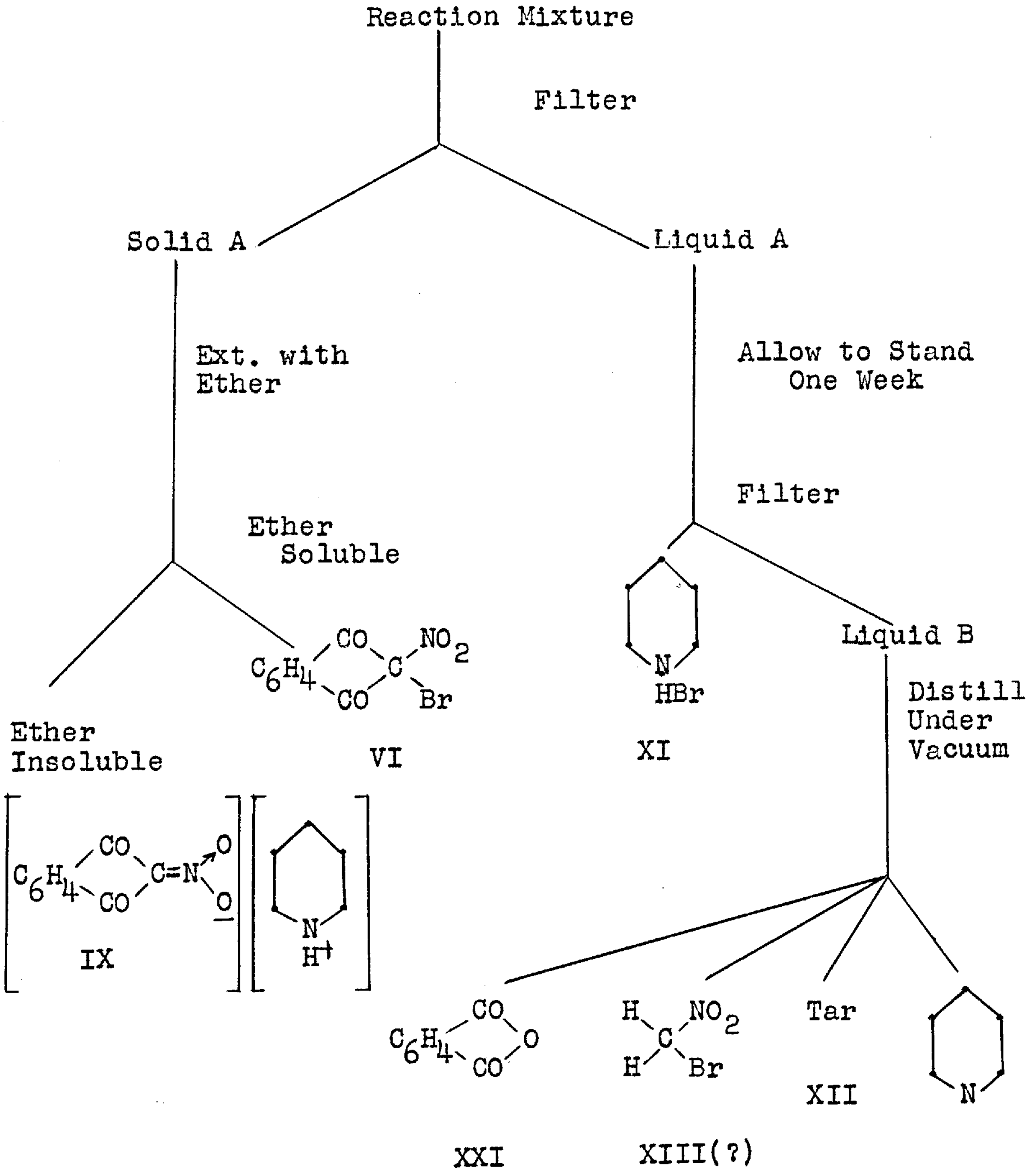
König (36,37,38) was working on a similar reaction which involved the ring splitting of pyridine, almost simultaneously with Zincke. König used cyanogen bromide rather than 2,4-dinitro-chloro-benzene to form the initial addition product with pyridine. The pyridinium salt was treated with an aromatic amine, usually aniline, and a dyestuff similar to Zincke's product was formed. These compounds were at one time considered as important dyestuffs for cotton. König was uncertain of the structure of his com-



pound and it was not until several years later that he assigned an open chain structure to the red colored dyestuff (39, 40).



Separation Scheme of the Reaction Mixture of 2-Bromo-2-nitro-1,3-indandione with Pyridine



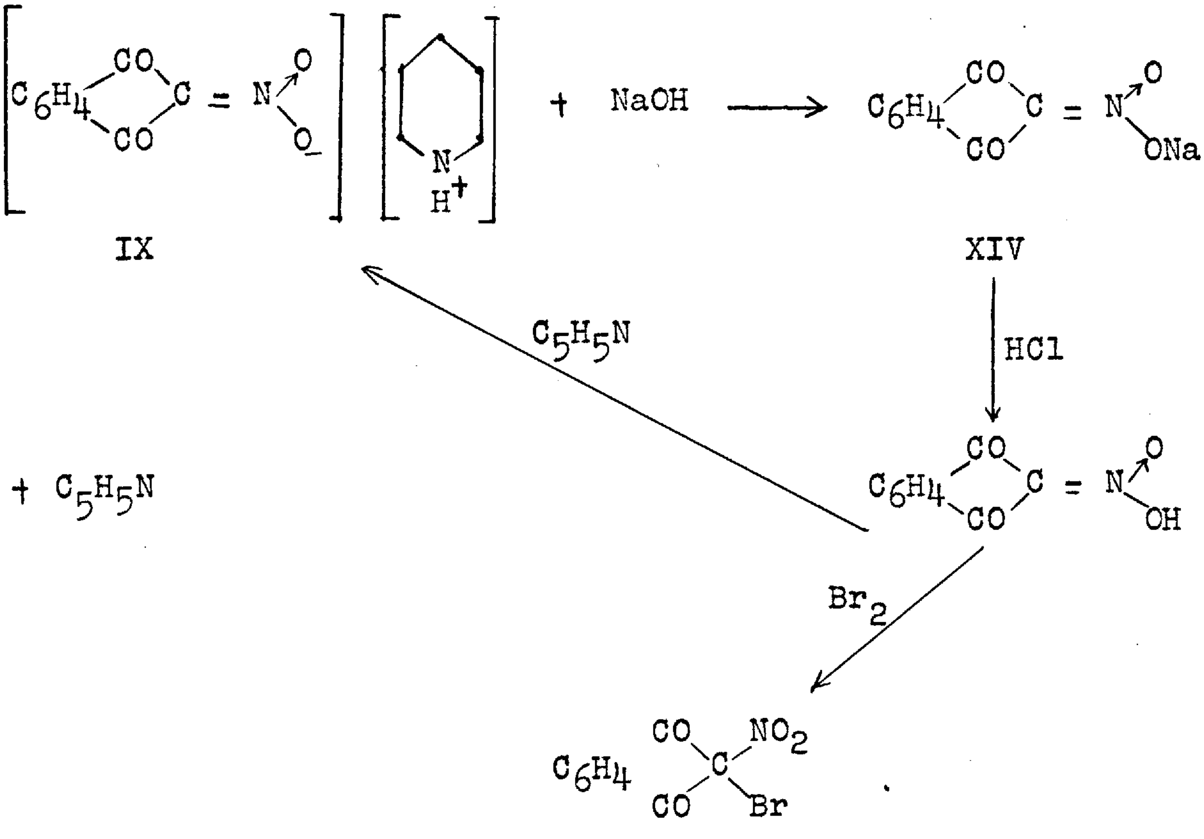
DISCUSSION

Reaction of 2-Bromo-2-nitro-1,3-indandione with Pyridine

(a) Reaction at room temperature

The reaction mixture from the interaction of 2-bromo-2-nitro-1,3-indandione and pyridine was separated according to the scheme on page 23. The Solid A which formed in the pyridine solution was separated into two fractions, the ether insoluble IX and the ether soluble VI. The ether insoluble portion IX had a melting point 169-170°C. It was analyzed for its elements and from the average values, carbon 62.28, hydrogen 4.03, nitrogen 10.74, the empirical formula was calculated as $C_{14}H_{10}O_4N_2$ which corresponded to a molecular weight of 270. However, molecular weight determinations gave a value of 229. IX was hydrolyzed with sodium hydroxide and the odor of pyridine was quite obvious; the pyridine was verified through its picrate. When concentrated hydrochloric acid was added to an alkaline solution of IX, yellow crystals of 2-nitro-1,3-indandione V formed which was identified by its bromo derivative and also its pyridine salt. This suggested that the yellow crystalline product was 2-nitro-1,3-indandione pyridinium salt and the hydrolysis could be explained by the following equations. The structure IX will be used throughout this thesis for the salts of

2-nitro-1,3-indandione, in keeping with the modern views of nitronic acid salts.


IX XIV VI

The theoretical value for the percentage of hydrogen in IX was calculated as 3.70; the analytical results obtained were all high, 4.03 being the average of six analyses. It was decided to check the analytical data and molecular weight with an authentic sample of the pyridinium salt prepared by the action of 2-nitro-1,3-indandione V on pyridine. This salt had a melting point 169-170°C. with decomposition and there was no depression with the sample IX obtained from the reaction of 2-bromo-2-nitro-1,3-indandione on pyridine. This authentic sample gave the following average values for its elements, carbon 62.28, hydrogen 3.85 and nitrogen 10.35. The percentage of hydrogen was again high and this was probably due to the fact that some of the oxides of nitrogen were not retained by the lead peroxide in the combustion tube but went through to the calcium chloride tube. The value for the molecular weight by the Rast method was 238. The low molecular weights showed that the pyridinium salt of 2-nitro-1,3-indandione was dissociated approximately 15% in camphor. It was hoped that it would be possible to compare the activity of IX as well as the authentic sample of the pyridinium salt toward the Grignard reagent in the Zerewitinoff apparatus. Unfortunately the pyridinium salts were not sufficiently soluble in the suitable solvents as pyridine, iso-amylether, n-butyl ether, dioxane, ethyl ether, tetrahydro furan, tetrahydro pyran; therefore the results were inconsistent and consequently unreliable.

The evidence amassed showed that the product IX was 2-nitro-1,3-indandione pyridinium salt.

Summary of data:

(a) No depression with an authentic sample in a mixed melting point.

(b) Molecular weight values and analytical results were similar for the reaction product IX and an authentic sample of 2-nitro-1,3-indandione pyridinium salt.

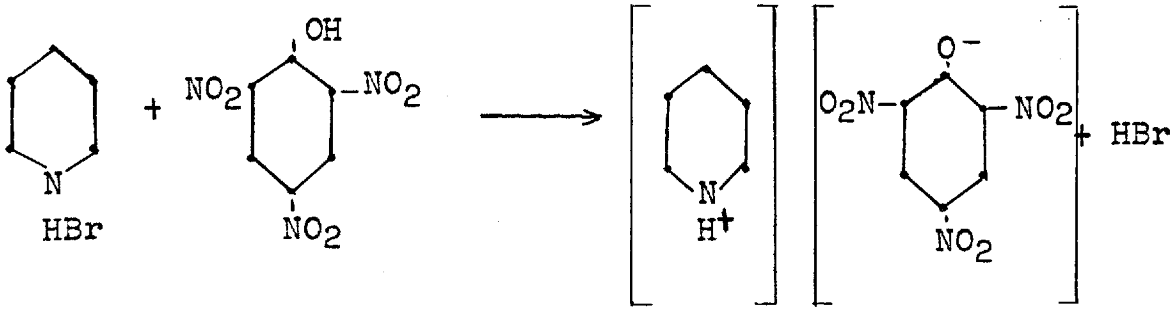
(c) Chemical evidence showed that IX was hydrolyzed into 2-nitro-1,3-indandione and pyridine which were identified by derivatives.

The remainder of Solid A consisted of the ether soluble fraction which melted at 111-112°C. It had a pungent odor resembling that of 2-bromo-2-nitro-1,3-indandione VI with which it gave no depression in a mixed melting point. The carbon and hydrogen values also checked for 2-bromo-2-nitro-1,3-indandione. It was observed when this material underwent combustion in the Pregl train it turned into a light green colored liquid after it melted. This was also observed when melting points were taken on 2-bromo-2-nitro-1,3-indandione. This phenomenon may be an indication that the pyrolysis of 2-bromo-2-nitro-1,3-indandione (12) could proceed by a free radical mechanism. The material which was isolated was unchanged starting material VI.

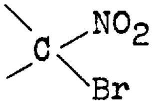
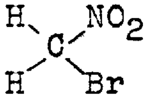
After Liquid A had stood undisturbed for about one week the formation of some brown crystals XI was observed. The almost black mother liquid was removed and the crude material was found to contain nitrogen and bromine. The crude brown crystals formed a picrate in which the absence of halogen was demonstrated. The picrate was analyzed for carbon and hydrogen and the values obtained approached the theoretical values of pyridine picrate, 43.00 carbon and 2.28 hydrogen. The result of the combustions were 43.02, 43.58 for carbon and 2.72, 2.78 for hydrogen.

The non-polar solvents like benzene, ether, dioxane, carbon tetrachloride were unsuitable for recrystallizing the crude pyridine hydrobromide XI. From 1,3-dibromo-propane the pyridine hydrobromide came down as a colorless microcrystalline material which melted 207-209°C. with decomposition. The halogen analyses gave values of 50.02 and 50.09 as compared to the theoretical value 49.93. Previously the crude pyridine hydrobromide had been analyzed for halogen and values of 48.05 and 47.07 were obtained.

It was quite obvious that picric acid was displacing the hydrogen bromide from pyridine as was demonstrated from analytical data and the absence of bromine in the picrate . The literature value for the melting point of pyridine hydrobromide is given by Trowbridge and Diehl (29) as 200°C. with decomposition.



The black liquid which remained after the pyridine hydrobromide XI was removed by filtration was distilled in vacuo. The pyridine distilled from 36-37°C. at 36 mm. of mercury; refractive indices were taken at intervals on the pyridine to check its purity. This was done in order to detect any other component which boiled at the same pressure and temperature. After the pyridine had been removed from the mixture, the vacuum was increased to 0.3 mm. and at a range between 33-40°C. a few drops of a lachrymatory liquid was collected in the receiver. The liquid was almost colorless and contained both nitrogen and bromine, however it was not obtained in an amount sufficient to purify or analyze quantitatively. This liquid did not form a picrate or mercuric chloride derivative which would indicate it was not a bromo-pyridine. Furthermore the liquid XIII was somewhat soluble in water and this aqueous solution was acidic to litmus; the aqueous solution did not give a precipitate with silver nitrate. The possibility arose that this material could be bromonitromethane which is also a lachrymator. A micro boiling point showed that the liquid boiled in the range of 140-145°C. with considerable darkening and decomposition. The boiling point of bromonitromethane in the literature was not very reliable. Victor Meyer and J. Tscherniak (41) reported 143-146°C., R.Scholl (42) gave 145-146°C., 715 mm., and later J. Tscherniak (43) reported the value as 147.5-149.5°C., 742 mm.

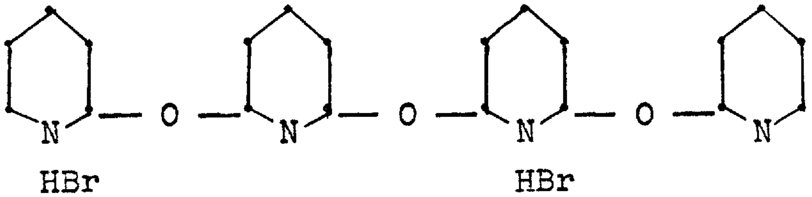
The action of concentrated alkali on XIII was to liberate ammonia. This would be possible if the material was bromonitromethane since concentrated alkali breaks down nitromethane into carbon dioxide and ammonia as was demonstrated by Wanag (3). 2-Bromo-2-nitro-1,3-indandione VI has a structure  similar to bromonitromethane  and it did not give a test for halogen in an aqueous solution. This was possibly due to its insolubility in water, though the aqueous solution was acidic because of a tautomeric change which imparts to primary and secondary nitro groups an acidic character. (Arndt and Rose (44)). The evidence is not sufficient to point conclusively to bromonitromethane as a reaction product of 2-bromo-2-nitro-1,3-indandione on pyridine but some qualitative tests indicated that the possibility should be considered.

During the vacuum distillation a considerable quantity of white needle-like crystals XXI formed in the neck and side arm of the distilling flask. These melted at 129-130°C. and did not contain nitrogen or bromine. The white crystals XXI were slightly soluble in water and imparted to water an acidic character. From the results of the analyses, carbon 64.43 and hydrogen 2.81, the empirical formula was found to be $C_8H_4O_3$ which is also the formula for phthalic anhydride. A mixed melting point with an authentic sample of phthalic anhydride showed no depression and the white crystals when heated with phenol and sulfuric acid formed phenolphthalein.

These results indicated that the crystals which formed in the distilling flask neck and side arm were phthalic anhydride. This was checked by several derivatives. The phthalic anhydride XXI was hydrolyzed to phthalic acid X and it was also converted to phthalimide XXII; the melting points of both derivatives checked the literature values. Even though the compound was proved to be phthalic anhydride it was possible that it could have been produced from phthalic acid during the vacuum distillation. Consequently, all the crude 2-nitro-1,3-indandione pyridinium salt IX which had accumulated from numerous reactions was extracted with ether; after the ether had been distilled off a white crystalline material remained which melted at 195-196°C. after recrystallization from ethyl alcohol. This material was suspected to be phthalic acid. It was treated with phenol and sulfuric acid and upon alkalization with sodium hydroxide it gave the pink color of phenolphthalein. It is a well known fact that if phthalic acid is heated above its melting point it will change into phthalic anhydride. This procedure was followed and phthalic anhydride crystals, m.p. 128-129°C. formed on the cold finger of the apparatus. The phthalic anhydride also underwent phenolphthalein formation with phenol. The conclusion was that phthalic acid was formed in the original reaction but the vacuum distillation transformed the acid into its anhydride.

The final product of the reaction of 2-bromo-2-nitro-1,3-indandione VI with pyridine was a black tar XII which remained in the distillation flask after all the pyridine, phthalic anhydride and the lachrymator were removed. This black substance could not be distilled or recrystallized. It contained both nitrogen and bromine; an aqueous solution of the hard black pitch-like substance gave an immediate precipitate with silver nitrate. A black tar was always a reaction product of the bromination of pyridine and was ignored for the most part by the workers in this field. McElvain proposed a polypyridyl type structure (page 18) for this polymer.

A complete analysis for its elements amounted to 89 percent (the remaining 11% assumed to be oxygen); therefore it differed from McElvain's compound. The fact that it contained pyridine was shown by the action of sodium hydroxide which released the of pyridine from this ? black polymer XII. The fact that it imparted an acidic character to water as well as containing an ionizable bromine indicated that it was a hydrobromide. The average values obtained for the elements were as follows: carbon 44.00, hydrogen 3.3, oxygen 11.1, nitrogen 10.1 and bromine 31.9. A structure could be proposed in which the pyridine nuclei were joined by oxygen bridges.



This type of compound would contain 46.2% carbon, 3.08% hydrogen, 9.24% oxygen, 10.08% nitrogen and 30.8% bromine. This black polymer which was always the main reaction product in bromination reactions of pyridine was never definitely proven and the above structure was merely advanced because the analytical data indicated its possibility.

Starting from 14 grams (0.52 M) of 2-bromo-2-nitro-1,3-indandione VI and 17 ml. (0.2 M) of pyridine the following products were obtained in the amounts indicated:

4.5 g. of 2-nitro-1,3-indandione pyridinium salt IX

3.1 g. of pyridine hydrobromide XI

0.1 g. of 2-bromo-2-nitro-1,3-indandione VI

1.24 g. of phthalic acid X corresponding to 1.1 g. of phthalic anhydride XXI

4.8 g. of the black polymer XII

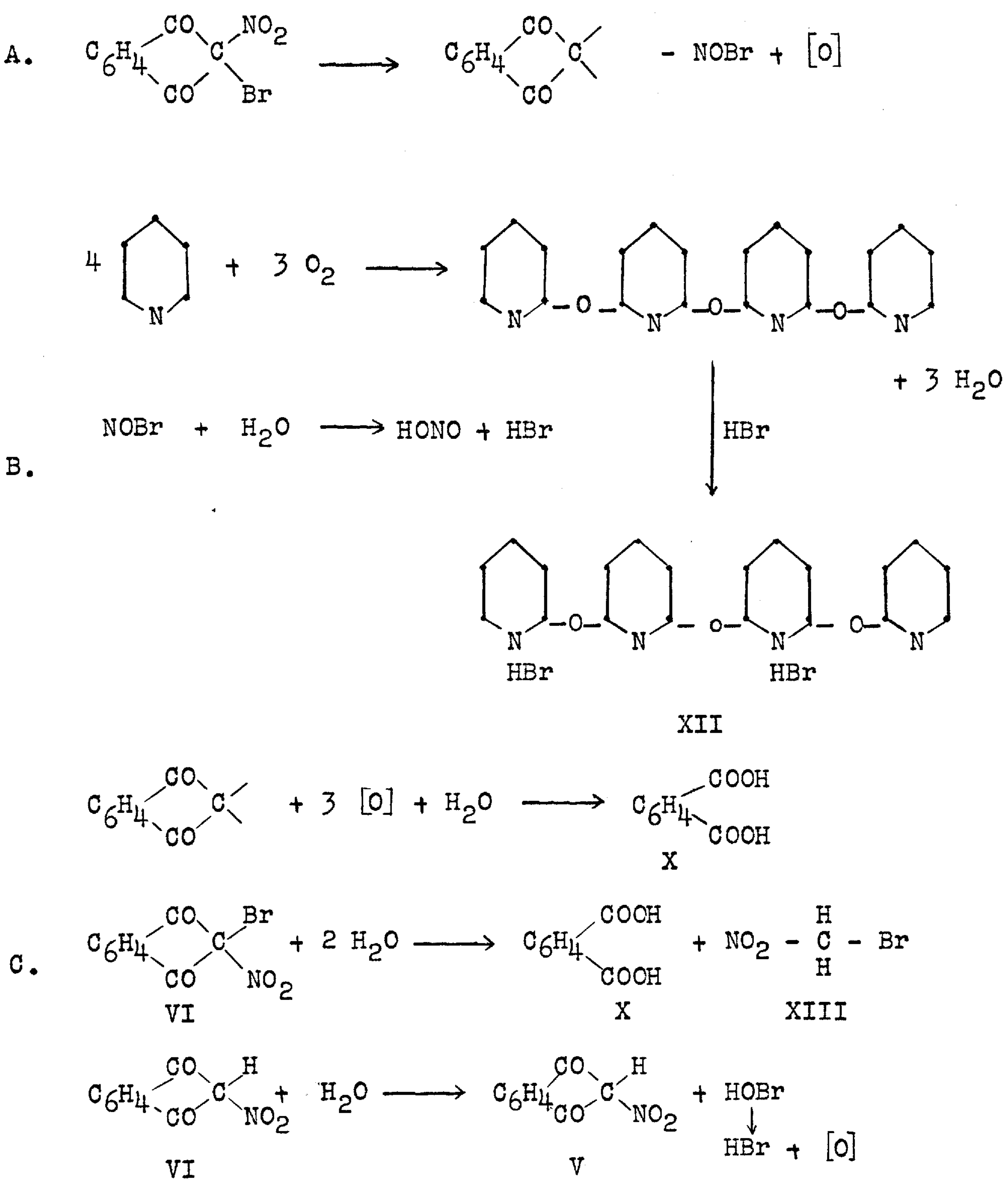
approximately 0.4 ml. of the lachrymatory liquid XIII

The starting material contained 4.15 grams of bromine and the total bromine content of the products was approximately 2.91 grams which was a 30 percent loss of bromine. It was observed during the reaction of 2-bromo-2-nitro-1,3-indandione VI with pyridine that starch-iodide paper inserted in the neck of the flask turned dark blue; this indicated that bromine and/or nitrosyl bromide was given off during the reaction. This gas evolution would account for the loss of bromine in the reaction.

It would be possible to write a series of equations which would account for the various products formed keeping in mind the behavior of 2-bromo-2-nitro-1,3-indandione when it was hydrolyzed (13) by Wanag and Bungs. These equations do not necessarily represent the only possible mechanism, but they follow routes suggested by known reactions of these bromo-nitro compounds.

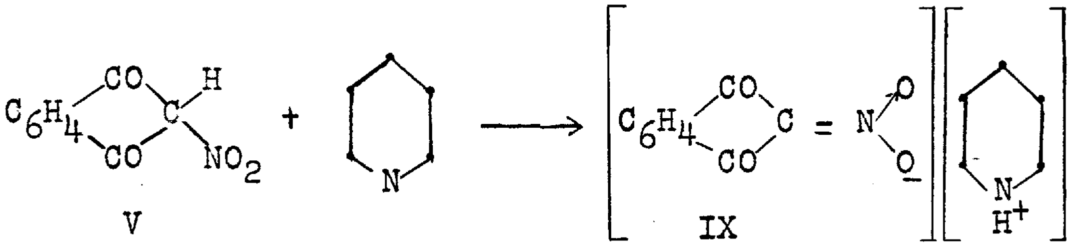
That 2-bromo-2-nitro-1,3-indandione is unstable to heat and moisture was shown by Wanag and Lode (12). The formation of a diradical would account satisfactorily for a source of oxygen which is necessary for the formation of the polymer XII and water, Equation B. The group of equations (C) explain the formation of phthalic acid X , the lachrymator XIII as well as 2-nitro-1,3-indandione V which is necessary for the main reaction product IX. It

Possible Mechanism for the Reaction of 2-Bromo-2-nitro-1,3-indandione with Pyridine

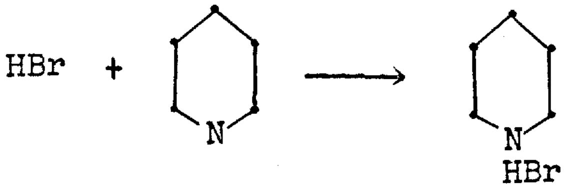


Possible Mechanism for the Reaction of 2-Bromo 2-nitro-1,3-indandione with Pyridine,(continued)

D.



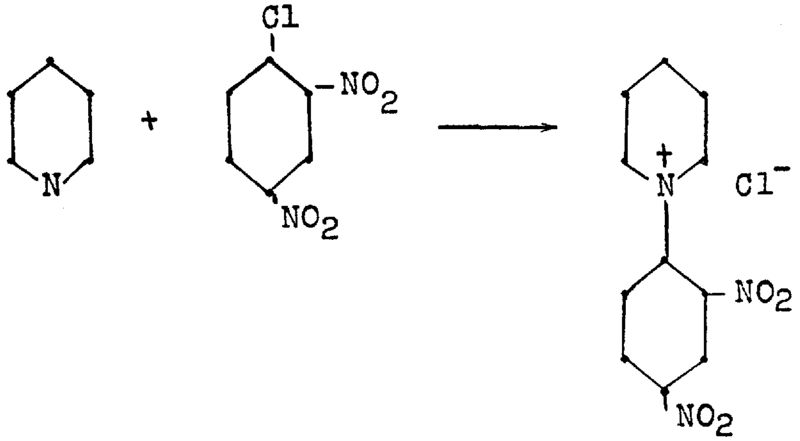
E.



XI

is well known that 2-bromo-2-nitro-1,3-indandione in the presence of noisture gives back the nitro derivative V which of course in the presence of excess pyridine would form the pyridinium salt, Equation D. The hydrogen bromide needed for the formation of the two salts XI and XII could arise from the hydrolysis of nitrosyl bromide or from the hypobromous acid.

The products obtained from the reaction clearly showed that 2-bromo-2-nitro-1,3-indandione did not form an addition compound with pyridine like dinitro-chlorobenzene which was discovered by Vongerichten and Spiegel (45, 46).



The halogen in 2-bromo-2-nitro-1,3-indandione was positive bromine which was easily demonstrated by its action with potassium iodide. The positive bromine oxidized the iodide to free iodine which was detected with starch. This behavior resembled that of N-bromo-succinimide and N-bromo-phthalimide.

(b) At reflux temperature of pyridine

The reaction of 2-bromo-2-nitro-1,3-indandione VI with pyridine was repeated at the reflux temperature of pyridine. The reaction was kept at this temperature for 2 hours and after cooling some reddish-brown crystals separated out. After recrystallization the product was yellow and melted at 169-170°C. with decomposition. A mixed melting point with an authentic sample of 2-nitro-1,3-indandione pyridinium salt gave no depression. The same major reaction product was obtained both at room temperature and at elevated temperatures. It was concluded that the isolated substance was IX. The pyridinium salt IX is sensitive to light and turns red after continuous exposure. The product was always tinted red after the high temperature reaction and this phenomenon was often observed when the product was obtained at room temperature. This sensitivity to light was also reported by Wanag and Lode (5).

Reaction of 2-Bromo-2-nitro-1,3-indandione with Alpha, Beta and Gamma Picoline

A partial investigation was made also of the reaction of 2-bromo-2-nitro-1,3-indandione on the various picolines. The reaction has already been studied with pyridine so it was expected that the main product in each case would be a picolinium salt. With alpha picoline the product XVI melted at 159.5-160.5°C. with decomposition. An authentic sample was then prepared by reacting 2-nitro-1,3-indandione with alpha picoline. This alpha picolinium salt had a melting point of 160-161°C. with decomposition. A mixed melting point of the two samples showed no depression , melting point 161°C. with decomposition. Wanag and Lode (5) reported the melting point of alpha picolinium salt of 2-nitro-1,3-indandione XVI as 161°C. with decomposition.

The reaction of 2-bromo-2-nitro-1,3-indandione VI on beta picoline yielded the beta picolinium salt XVIII, melting point,145-146°C. with decomposition. An authentic sample was prepared by treating 2-nitro-1,3-indandione with beta picoline . The product XVIII melted at 145-146°C. No depression was observed with a mixed melting point.

Finally gamma picoline was treated with 2-bromo-2-nitro-1,3-indandione VI and the expected 2-nitro-1,3-indandione gamma picolinium salt XX was the product, melting point 172-173°C. with decomposition. A mixed melting point with an authentic sample of the gamma picolinium salt showed no depression, melting point 172-173°C. with decomposition.

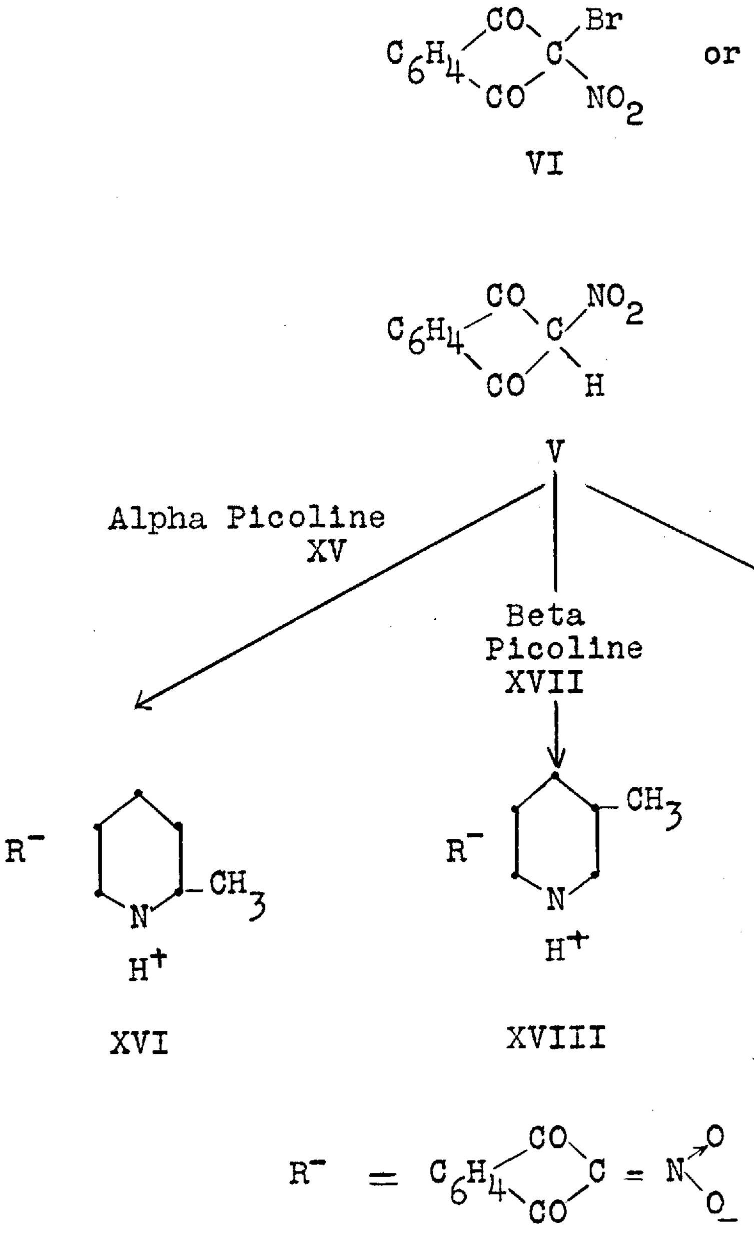
The above mentioned picolinium salts are reported by Christensen and his co-workers (6) and in most instances his values are lower than the values above as well as a few others which appear later in this discussion.

TABLE I

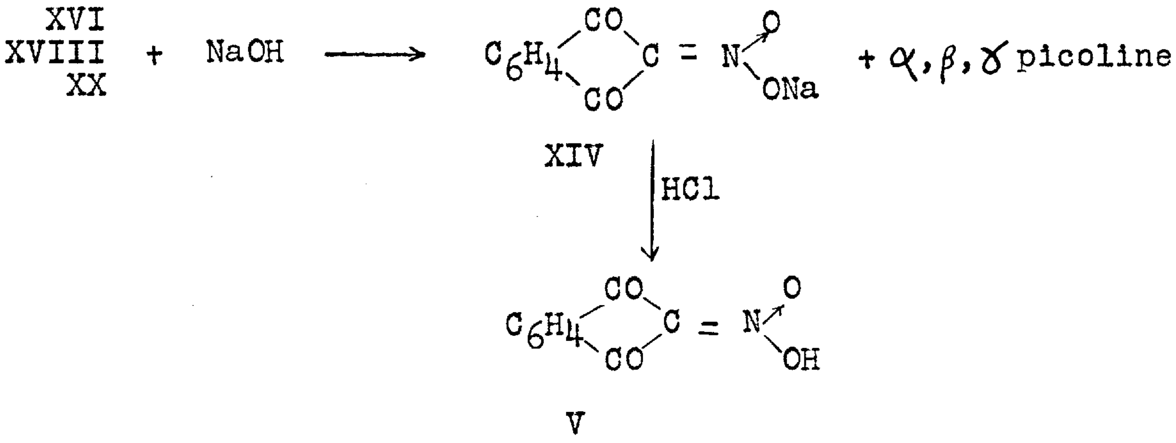
Comparison of Melting Points of Some 2-Nitro-1,3-indandione Derivatives

	Christensen (6) and co-workers	Wanag and Lode (5)	This Investigation
Pyridine	166-168°C.	169-170°C.	169-170°C.
Alpha Picoline	147-148°C.	161°C.	160-161°C.
Beta Picoline	141°C.	---	145-146°C.
Gamma Picoline	160-162°C.	---	172-173°C.
Aniline	185-187°C.	209°C.	208-209°C.
Orthotoluidine	185-186°C.	197-198°C.	210-211°C.
Cyclohexyl Amine	221-222°C.	213°C.	209-210°C.

These reactions clearly showed that the main reaction product was the same if either 2-nitro-1,3-indandione V or 2-bromo-2-nitro-1,3-indandione VI was allowed to react with the picolines.

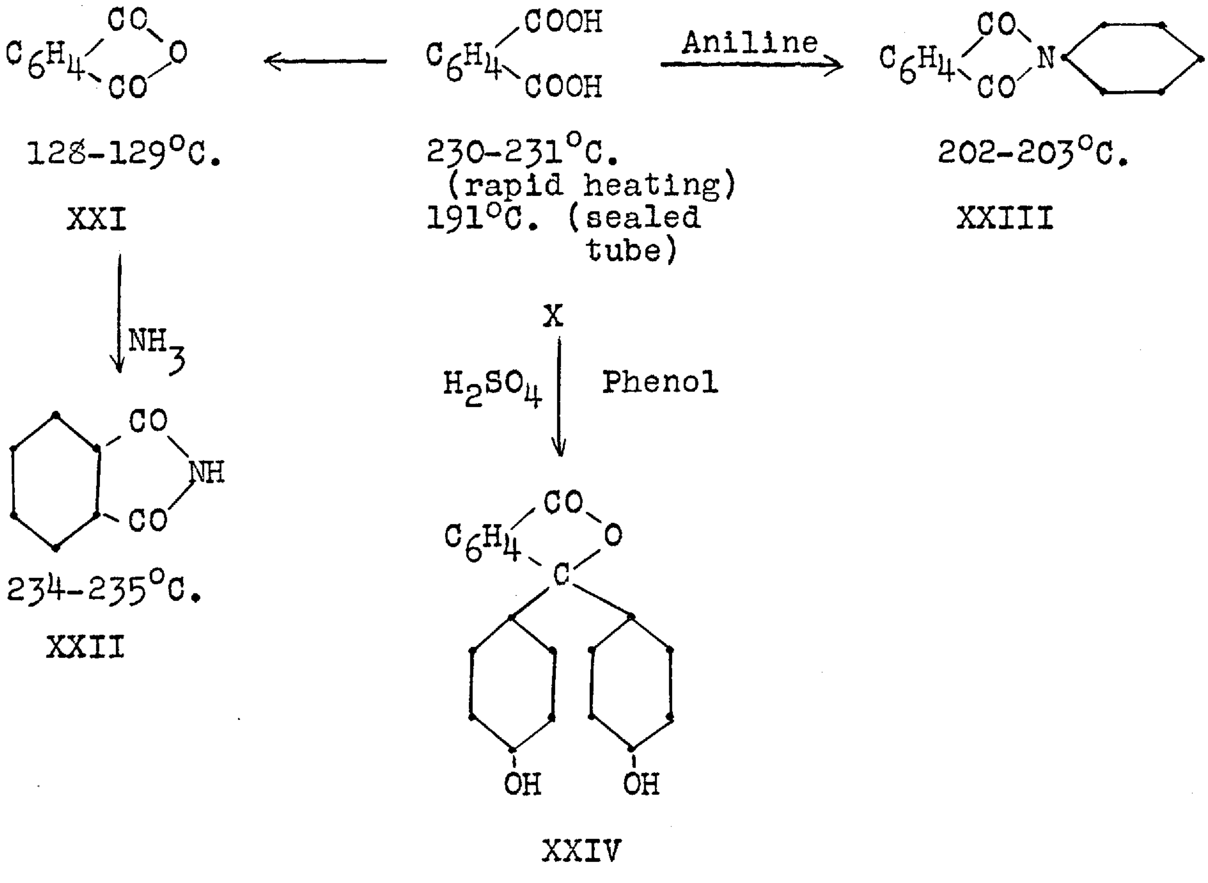


The picolinium salts XVI, XVIII and XX were treated with sodium hydroxide which cleaved off the picoline component. The action of concentrated hydrochloric acid on the alkaline solutions of the picolinium salts caused the yellow crystals of 2-nitro-1,3-indandione to form as was the case with pyridinium salt IX.



By-product of Bromination of 2-Nitro-1,3-indandione

The bromination of 2-nitro-1,3-indandione V was accomplished by a procedure which was given by Wanag (3). This method consisted of adding bromine water to an aqueous solution of 2-nitro-1,3-indandione. Wanag and Lode (5) claimed a yield of 98.9% of 2-bromo-2-nitro-1,3-indandione. A re-check of their calculations showed an error in the reported yield; they actually had a yield of 78% rather than 98.9%. This meant that a considerable portion of the 2-nitro-1,3-indandione was unaccounted for in the reaction. The mother liquor from the bromination was evaporated down to dryness and long white crystals remained in the beaker which melted at 230-231°C. when heated rapidly, and 191°C. in a sealed tube which is indicative of phthalic acid. The crystals resembled phthalic acid in appearance and they formed phenolphthalein when treated with sulfuric acid and phenol. The phthalic acid was verified by preparing N-phenyl phthalimide by its reaction with aniline and the phthalic acid was changed into phthalic anhydride by heating it above its melting point. By passing ammonia gas into the molten phthalic anhydride, phthalimide was produced.



128-129°C.
XXI

230-231°C.
(rapid heating)
191°C. (sealed tube)

202-203°C.
XXIII

234-235°C.
XXII

XXIV

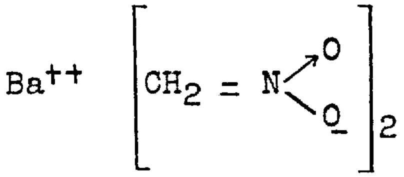
The yield of phthalic acid from the bromination of 2-nitro-1,3-indandione was 1.8 g. This production of phthalic acid from the bromination of 2-nitro-indandione was completely overlooked previously, due to an error in the workers' (5) calculations.

In order to show that the 2-bromo-2-nitro-1,3-indandione VI which was used in these studies was not contaminated with phthalic acid, its purity was checked. The presence of phthalic acid as a contaminent would account for its isolation as a reaction product. Therefore a portion of the 2-bromo-2-nitro-1,3-indandione was heated in a sublimation apparatus above its melting point. When VI had melted it turned into a light green colored liquid and continued heating did not produce any needle-like crystals on the cold finger. An additional check was made by heating 2-bromo-2-nitro-1,3-indandione VI with phenol and sulfuric acid. When the acid solution was made alkaline with sodium hydroxide the solution did not give the pink color of phenolphthalein which would have been produced by phthalic acid or phthalic anhydride. From this it was concluded that the phthalic acid which was isolated from the reaction of 2-bromo-2-nitro-1,3-indandione was not present in the starting material as an impurity.

Electronic Structure of 2-Nitro-1,3-indandione and 2-Bromo-2-nitro-1,3-indandione

Wanag and Gudrinieze (11) reported that 2-nitro-1,3-indandione V did not give a color reaction with ferric chloride in an aqueous solution. However, it was observed that when the sodium salt of 2-nitro-1,3-indandione XIV was acidified the 2-nitro-1,3-indandione which resulted gave an intense violet coloration with a solution of ferric chloride. According to Hantzsch (47), Hantzsch and Veit (48) a primary or secondary nitro compound is always acidic and can be transformed into a salt by a strong base. The neutralization is a slow reaction and the rate can be measured in the following way. The conductivity of an aqueous solution of nitro methane is very small because it is slightly ionized. If barium hydroxide is added the conductivity rises to a value which is observed if the nitro compound is not present; however, the conductivity decreases gradually until it reaches the value of the salt.

CH_3NO_2

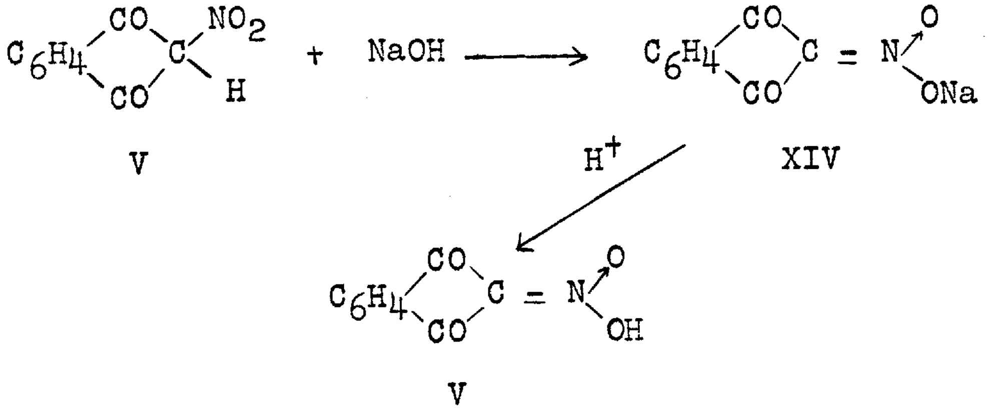


$$Ba^{++} \left[CH_2 = N \begin{matrix} \nearrow O \\ \searrow O^- \end{matrix} \right]_2$$

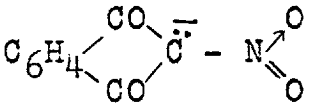
The regeneration of the nitro compound is also slow; when an equivalent quantity of hydrogen chloride is added to a solution of the salt, the conductivity is initially high but decreases shortly to the conductivity due to the barium chloride. The reaction between the salt and the strong acid is weakly acidic immediately after the addition of exactly the equivalent amount of hydrogen chloride because of the nitronic acid which is formed. It may be inferred therefore that the nitro compound can exist in two distinct forms. The normal form is less acidic; the other which is called the aci form is the less stable but more acidic of the two. In an aqueous solution nitro methane is largely in the relatively non-acidic form; when the salt is treated with hydrogen chloride, the aci form is rapidly produced which rearranges to the stable normal form.

It was decided to check the reaction of nitro ethane and nitro propane with ferric chloride solution. Both of these nitro compounds are essentially neutral but when water was added the solutions became acidic to litmus paper but neither gave a color reaction with ferric chloride. The solutions of both nitro ethane and nitro propane were treated with a slight excess of sodium hydroxide and then acidified with hydrochloric acid. A deep violet coloration was given by both when ferric chloride was added. Hantzsch (47) and Arndt and Rose (44) had shown that certain arylnitromethanes yielded on acidification of their alkaline solutions, solid aci- forms which were more acidic than the normal forms, and from which, furthermore, they were sharply distinguished by intense color reactions with ferric chloride, and unsaturation towards bromine.

This proved that the nitro group after it had undergone a tautomeric change reacted with ferric chloride in a similar way to enols. From these observations it was concluded that 2-nitro-1,3-indandione in an aqueous solution existed largely as the nitro ketone and not the nitro enol or nitronic acid which would react with ferric chloride. The coloration with ferric chloride after acidification of the sodium salt could be attributed to nitronic acid structure.



Wanag and Bungs (9) concluded that in an aqueous solution, 2-nitro-1,3-indandione existed in the aci- form. They reached this conclusion from the results they obtained from Meyer titrations. This method depends on the fact that the nitro-keto form will not react with bromine unless it is changed into the enol form. The above workers are not justified therefore, in reaching their conclusion based on the titration data. Bases react with 2-nitro-1,3-indandione to form an anion which is stabilized by different resonating structures. Salt formation and bromination proceeds through these resonance structures at the moment when reaction occurs. On the basis of experimental evidence and the modern views of keto-enol and nitro-aci nitro structures, the following interpretation of the electronic structure of 2-nitro-1,3-indandione is advanced.



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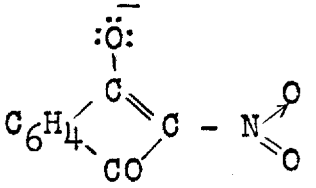

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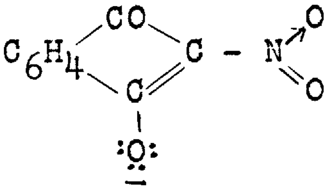

C

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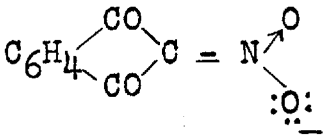

D

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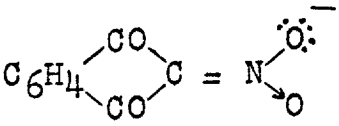
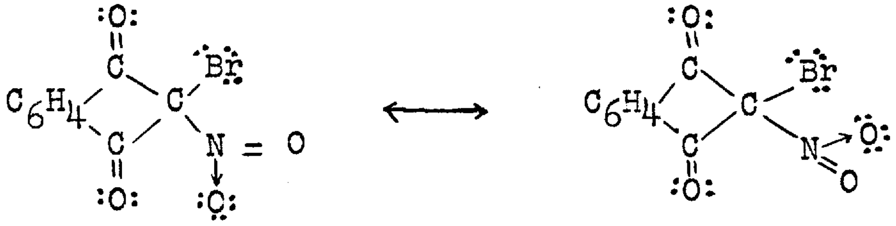


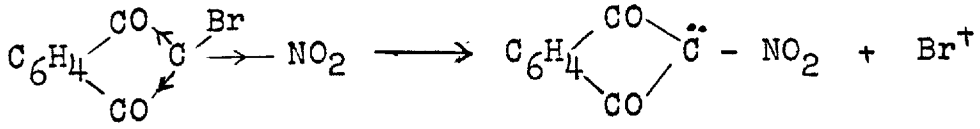
E

One of these structures, A, is a carbanion, two, B and C, are enolate and two, D and E, are nitronic acid anion structures.

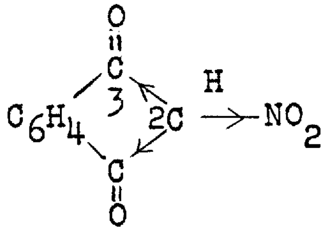
The situation was quite different with 2-bromo-2-nitro-1,3-indandione because the possibility for the existence of the enol and aci forms had been removed.



The electronic structure of 2-bromo-2-nitro-1,3-indandione indicates a very high electron density in the molecule. The strong polarization which exists in this molecule due to the electron attraction of the carbonyl and nitro groups holds an electron pair at the carbon atom number 2. The bromine atom can therefore react as a positive halogen.



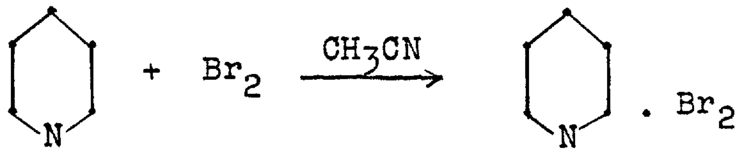
In 2-nitro-1,3-indandione, there is a permanent polarization; the C - H bond at carbon atom number two is weakened by 2 carbonyl and one nitro group.



Reaction of Bromine on Pyridine in Acetonitrile

The action of cyanogen bromide on pyridine caused the pyridine ring to be ruptured in a remarkable manner. Glutaconaldehyde was isolated from this reaction as the dianil because of the glutaconaldehyde's instability. This reaction suggested the possibility of ring opening with bromine in an inert solvent and that the subsequent addition of aniline would give the dianil of glutacondialdehyde. One would not expect any bromo pyridines from this reaction because the pyridine ring is attacked only at much higher temperatures.

When equimolar quantities of pyridine and bromine were allowed to react with each other in acetonitrile, the reaction gave off considerable heat and the solution was deep red in color. If this liquid was poured into cold water, orange-red crystals formed (m.p., 61-63°C.). These crystals were suspected of being pyridine perbromide.



XXV

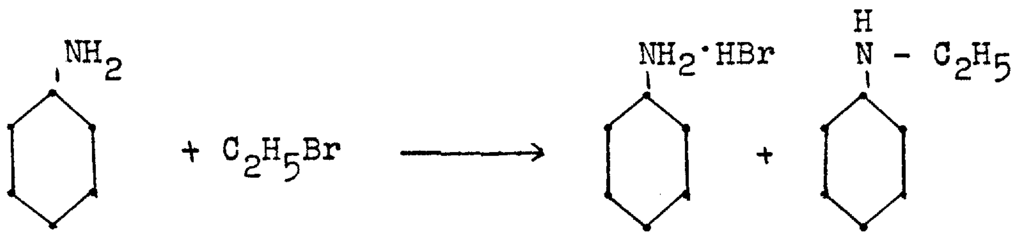
The red crystals XXV formed a picrate which contained no halogen which showed that the bromine was not on the pyridine ring. The picrate showed no depression with an authentic sample of pyridine picrate. The pyridine perbromide XXV could not be recrystallized and it decomposed after 36 hours with evolution of bromine, into a dark brown solid mass.

The usual method of preparing pyridine perbromide was according to Williams (32) and a sample was prepared in order to compare it with the product of the above method. The method was somewhat similar except that carbon tetrachloride was the solvent and that the pyridine perbromide precipitated out rather than remaining in solution. The product of this reaction, pyridine perbromide, was also an orange-red solid, (m.p. 62-63°C.). There was a difference in stability of the two products; pyridine perbromide prepared in acetonitrile decomposed after 36 hours and if it were prepared according to Williams' procedure, it decomposed after 20 hours. A mixed melting point of the two samples was found to be 62-63°C. The yields were almost identical, 40% by

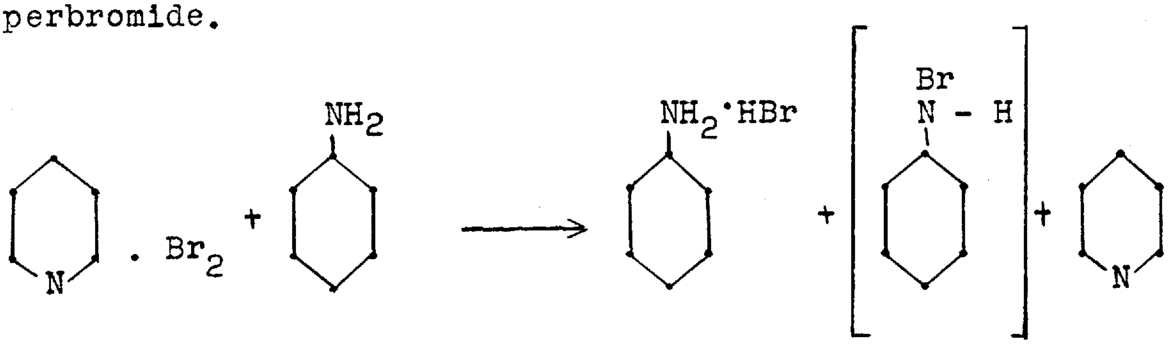
Williams' method and 33% in acetonitrile as the solvent. It was observed that pyridine perbromide could be stored a week and longer if kept in water at 0°C. The solution of pyridine perbromide in acetonitrile was also stable if kept in the refrigerator.

Reaction of Pyridine Perbromide on Amines

The acetonitrile solution of pyridine perbromide formed a red crystalline product with aniline which had no definite melting point (m.p. $>200^{\circ}C.$ $<270^{\circ}C.$) . The analytical data gave following average values, carbon 41.15, hydrogen 4.4, nitrogen 8.24, and bromine 45.54. These values gave an empirical formula $C_6H_8N_1Br_1$ which is also the formula for aniline hydrobromide. The red crystals could be diazotized which meant it contained a free amino group. The possibility for the bromine being situated on the nitrogen was eliminated since it did not oxidize iodide to iodine which is a typical reaction for N-bromo compounds. The halogen in the compound was easily removed as it gave a precipitate with silver nitrate. It was discovered that if the red product was treated with Norite the color was removed even though repeated recrystallizations gave a red product in the absence of charcoal. The aniline hydrobromide XXVI formed a 2-nitro-1,3-indandione derivative, m.p. 208-210°C. with decomposition. The same value was obtained for the 2-nitro-1,3-indandione derivative prepared from a sample of aniline hydrobromide which was obtained by reacting aniline with hydrobromic acid. The red color which was evident was probably due to a side reaction which contaminated the product. Hoffman (49) reported a brownish yellow specimen of aniline hydrobromide from the reaction of ethyl bromide with aniline.

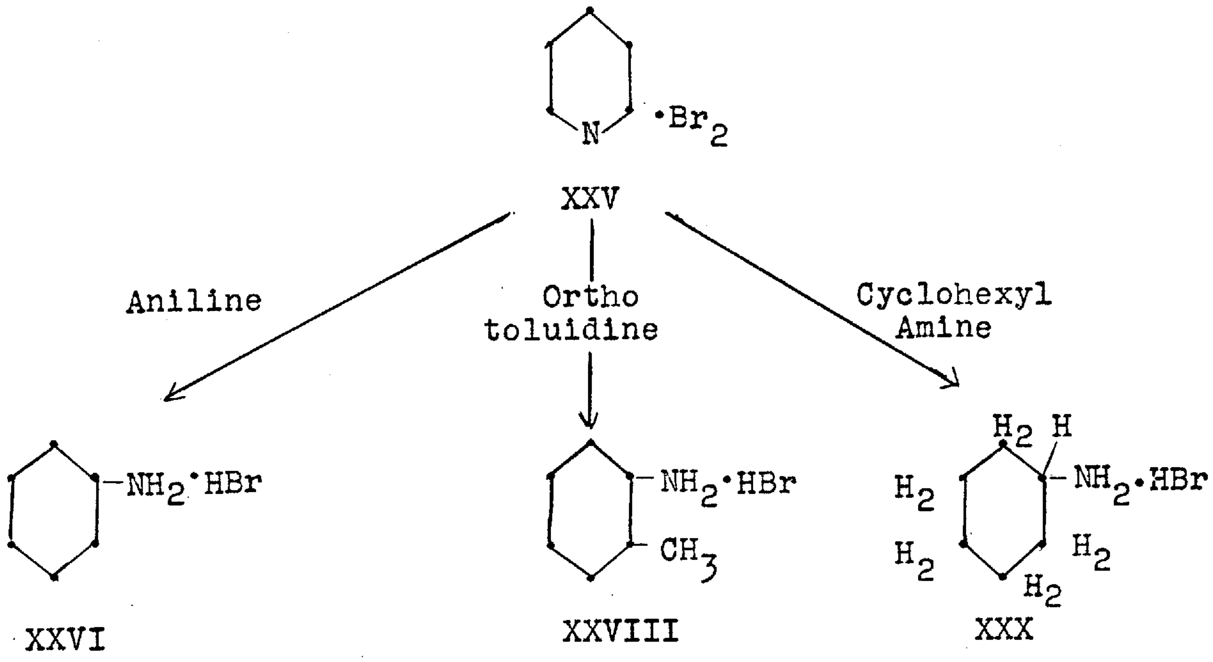


A similar equation can be written to account for the observed reaction product using aniline and pyridine perbromide.



The hypothetical intermediate was not isolated. However, the fact that the aniline hydrobromide was colored red before purification indicated that this was not the sole reaction product. The side reaction was not investigated at this time.

In order to see whether this was a general reaction for amines it was repeated with ortho-toluidine. The ortho-toluidine hydrobromide XXVIII as it formed was a light blue-gray solid which by repeated recrystallizations from acetic acid with Norite became a pure white material. The melting point of the ortho-toluide hydrobromide as well as its 2-nitro-1,3-indandione derivative agreed with values obtained with a sample prepared from ortho-toluidine and hydrobromic acid. The reaction worked equally well with a non-aromatic amine. The expected cyclohexyl amine hydrobromide XXX was obtained from the the interaction of pyridine perbromide and cyclohexyl amine.



There does not appear to be a relationship between the amount of the amine hydrobromide produced and the basicity of the amine as can be seen from the following table.

TABLE II

Comparison of Yield of the Salt with the Basic Strength of the Amine

Amine	Mol. Wt.	Wt. of Amine Used	Ionization Constant	Yield
Aniline	93	3.0 g.	4×10^{-10}	2.0 g.
Ortho-toluidine	107	3.0 g.	2.5×10^{-10}	0.65 g.
Cyclohexyl Amine	99	3.0 g.	4.39×10^{-4}	3.0 g.

EXPERIMENTAL

The analyses were performed in the Organic Analytical Laboratory of the McGill University Chemistry Department by the author. All determinations were in duplicate unless otherwise indicated. Halogen and carbon and hydrogen analyses were done on a semi-micro scale; the Dumas Method for nitrogen was carried out as a micro determination.

Preparation of 1,3-Indandione

Over a period of 2 hours 2.4 M of ethyl acetate was added drop by drop to a mixture of 1 M of ethyl phthalate and 2 M of sodium sand. The reaction flask was heated to reflux temperature in an oil bath for 7 hours and during this interval the contents of the flask turned solid. Ethyl alcohol was used to destroy any unused sodium. The product, a yellow sodium salt, was dissolved in 1.5 to 2 liters of hot water and filtered while still warm; the sodium salt precipitated out immediately. The yield was 185 g. (77% of the theoretical).

The sodium salt of 2-carbethoxy-1,3- indandione I was transformed into the desired product, 1,3-indandione III by the following method. Forty grams of the sodium salt was placed in a paraffin lined porcelain dish and stirred with 25 ml. of 4 N sulfuric acid for one half hour, after which time the contents were transferred with 4 N sulfuric acid into a beaker. The suspension was heated on a water bath to 60-65°C. until gas evolution had ceased, then it was cooled to 55°C. and filtered rapidly into a receiver. The product was a white or soft yellow micro-crystalline powder, m.p. 129-131°C. The yield was 10 g. or 40% of the theoretical.

The decarboxylation, even with careful temperature control, always resulted in the formation of some bindone (anhydro-bisindandione)IV. Bindone was a light brown or tan solid which melted 195-200°C. From 40 g. of the sodium salt of 2-carbethoxy-1,3-indandione I the yield of bindone was 18 g. A color reaction was used to identify the bindone; a deep blue color was produced immediately when bindone was added to a solution of aniline in acetic acid.

The Nitration of 1,3-Indandione

A 5 g. sample of 1,3-indandione III was dissolved in 50 ml. of glacial acetic acid and to this cooled solution was added gradually a mixture of 5 ml. of fuming nitric acid and 15 ml. of glacial acetic acid. The mixture was cooled with running water and almost immediately the yellow product, 2-nitro-1,3-indandione V, appeared. The product was filtered under suction and recrystallized from acetic acid. The slightly yellow colored crystals were obtained in an 87% yield, 6.7 g. (m.p. 113-114°C.). The melting point of 2-nitro-1,3-indandione V did not always check the literature value of 113-114°C.; the yellow crystals often melted a few degrees higher.

Bromination of 2-Nitro-1,3-indandione

To an aqueous solution containing 15 g. of 2-nitro-1,3-indandione V, bromine water was added slowly and with stirring until the excess of bromine was evident by its brown color. The solution was cooled in an ice bath for one hour; the white product was filtered, washed with cold water, then dissolved in ether and dried with sodium sulfate. After the ether was removed, the white crystals of 2-bromo-2-nitro-1,3-indandione VI appeared. The product melted at 110-112°C. The same melting point was observed if the product was dried in a vacuum over phosphorus pentoxide without dissolving in ether and drying with sodium sulfate. In moist air the substance was yellow because of the loss of bromine from the re-formed 2-nitro-1,3-indandione. Starting with 15 g. of 2-nitro-1,3-indandione the product which was obtained weighed 14.5 g., or a yield of 68.5%.

Phthalic Acid from the Bromination of 2-Nitro-1,3-indandione

After the 2-bromo-2-nitro-1,3-indandione VI was removed by filtering the cold solution, the filtrate which usually amounted to about 2 liters of solution was evaporated down to dryness on a steam bath. An examination of the long white needle-like crystals indicated that they were phthalic acid X. The absence of halogen and nitrogen was confirmed by sodium fusion tests. In the electric melting point apparatus with rapid heating the melting point was 230-231°C.; in a sealed tube the melting point was 189-190°C. The literature value of phthalic acid is given as 191°C. (sealed tube) and 231°C. with rapid heating. The crystals, when treated with phenol and sulfuric acid, gave the pink color of phenolphthalein XXIV when made alkaline.

About 0.1 gram of the phthalic acid X was heated with 0.5 g. of aniline for 3 minutes and then poured into a 1:1 mixture of water and alcohol. The white flaky precipitate which formed was recrystallized from ethyl alcohol. The melting point was 202-203°C. The melting point of N-phenylphthalimide XXIII in the literature is 204-205°C.

A portion of the phthalic acid X was heated to 200°C. in a sublimation apparatus; long white needle-like crystals formed on the cold finger which melted at 128-129°C. The recorded melting point of phthalic anhydride XXI is 130°C.

The phthalic anhydride XXI from above was heated slightly above its melting point and ammonia gas was passed over the molten mass. The product which formed melted at 234-235°C. The literature value for phthalimide XXII is 234-235°C.

Reaction of 2-Bromo-2-nitro-1,3-indandione with Pyridine at Room Temperature

The pyridine which was used for this investigation was dried over barium oxide and distilled from potassium hydroxide.

The reaction flask was a 100 ml. 3 neck flask which was equipped with a mechanical stirrer, thermometer, dropping funnel and an inlet for nitrogen gas. The ratio of pyridine to 2-bromo-2-nitro-1,3-indandione VI was 4:1. 0.052 M (14 g.) of 2-bromo-2-nitro-1,3-indandione was placed in the flask which had a continuous flow of nitrogen passing through it. The dry pyridine, 0.20 M (15.8 g.), was added drop by drop. After all the pyridine was transferred to the reaction flask, the solution was yellow in color and some yellow solid material was already formed. Stirring was continued for 4 hours; during this interval no appreciable temperature change had occurred since the final temperature was usually only about 4 degrees higher than the initial temperature.

The reaction flask was placed in the refrigerator overnight, after which the Solid A was removed by filtering. The filtrate continued to cloud up after removing Solid A and more crystals continued to form. It was necessary to filter 7 or 8 times to completely remove Solid A which was then extracted with ethyl ether in a Soxhlet Extractor. This extraction process gave an ether soluble fraction VI and an ether insoluble portion IX. The Liquid A was allowed to stand one week.

(a) Investigation of Solid A

The ether insoluble fraction 2-nitro-1,3-indandione pyridinium salt IX was a yellow crystalline solid which after several recrystallizations from ethyl alcohol had a very fine plate-like structure and melted at 169-170°C. with decomposition. IX could also be recrystallized from water and if the aqueous solution was allowed to stand overnight the crystals grew in large clusters which were transparent. These crystals also melted at 169-170°C. with decomposition. A sodium fusion on IX showed the absence of bromine. A 10% solution of sodium hydroxide on IX gave the unmistakeable odor of pyridine. A mixed melting point with a sample of pyridinium salt prepared from 2-nitro-1,3-indandione and pyridine gave no depression. The authentic sample melted at 169-170°C. with decomposition.

<u>Anal</u>. Calcd. for $C_{14}H_{10}O_4N_2$: carbon 62.23; hydrogen 3.70;

nitrogen 10.38.

Found: carbon 62.27, 62.05, 62.20, 62.39, 62.20, 62.60; hydrogen 3.99, 4.04, 4.06, 4.00, 4.08, 4.02; nitrogen (Dumas) 10.33, 11.05, 10.29.

Molecular weight: Calcd. 270. Found by Beckmann cryoscopic method 179; by Rast method 229.

The ether was distilled off the ether soluble component of Solid A. The product which remained, 2-bromo-2-nitro-1,3-indandione VI was recrystallized twice from ethyl alcohol from which VI came down as a white solid. The product weighed 0.1 g. and melted at 111-112°C. A mixed melting point with an authentic sample of 2-bromo-2-nitro-1,3-indandione showed no depression, m.p. 111-112°C.

Anal. Calcd. for $C_9H_4O_4N_1Br_1$: carbon 40.02; hydrogen 1.49.

Found: carbon 40.74, 40.31; hydrogen 1.65, 1.73.

(b) Investigation of Liquid A

After Solid A had been removed by filtration from the reaction mixture the Liquid A was allowed to stand for a week at room temperature; during this period of time the solution which was originally light yellow turned into a very dark liquid. It was observed that some light brown colored crystals XI had formed in the dark viscous solution. Early attempts to recrystallize these brown crystals were unsuccessful because of their extreme solubility in polar solvents and their insolubility in non-polar solvents. A sodium fusion on XI pyridine hydrobromide showed that both nitrogen and bromine were present. The crude pyridine hydrobromide was extracted with ethyl ether in a Sohxlet apparatus to remove any ether soluble contaminents and after this treatment the light brown crystals melted at 195-200°C. The yield was 2.2 g. Pyridine hydrobromide XI formed a picrate with picric acid in which the picrate replaced the hydrobromide. The pyridine picrate was analyzed for carbon, hydrogen and nitrogen rather than the crude product XI. The picrate formed readily as bright yellow crystals, m.p. 163-164°C. A mixed melting point with pyridine picrate showed no depression.

Anal. calcd. for $C_{11}H_8O_7N_4$: carbon 43.00; hydrogen 2.28; nitrogen 18.18.

Found: carbon 43.58, 43.05; hydrogen 2.72, 2.78; nitrogen (Dumas) 18.00, 17.40.

The Carius analysis for bromine was done on the crude material XI.

Anal. Calcd. for $C_5H_6N_1Br_1$: Bromine 49.93.

Found: 48.05, 47.07.

Finally it was observed after trying various solvents that pyridine hydrobromide XI could be recrystallized from 1,3-dibromopropane. After recrystallization the product XI was a pure white powder which melted at 207-209°C. The literature value for the melting point of pyridine hydrobromide is given as 200°C. The recrystallized product was analyzed for bromine.

Anal. Calcd. for $C_5H_6N_1Br_1$: bromine 49.93.
Found: bromine 50.02, 50.09.

(c) Investigation of Liquid B

The dark brown pyridine solution which remained after the removal of pyridine hydrobromide XI was distilled. The pyridine VIII distilled over 36-37°C. at 36 mm. of mercury; refractive indices were taken at intervals to make certain no other products were distilling over. The value of the refractive index of the distillate was 1.5075 as compared to 1.5091 given in the literature for pyridine. When the pyridine ceased coming over, the vacuum was increased to 0.3 mm. of mercury and immediately the white needles of phthalic anhydride XXI began to form in the neck and side arm of the distilling flask. The temperature during this sublimation varied from 28-32°C. At 33-40°C./0.3mm., approximately 0.1 ml. of a liquid XIII came over into the receiving flask and a black tar XII remained in the distilling flask which would not distill.

(i) The phthalic anhydride XXI which formed in the neck and arm of the distilling flask was removed and purified by subliming it under reduced pressure. After sublimation the phthalic anhydride was recrystallized twice from ethyl alcohol. The yield was 1.1 g., m.p. 129-130°C.

Anal. Calcd. for $C_8H_4O_3$: carbon 64.81; hydrogen 2.70.
Found: carbon 64.50, 64.37; hydrogen 2.81, 2.82.

About 0.1 gram of phthalic anhydride XXI was dissolved in a minimum of water and an excess of ammonium hydroxide was added. The solution was evaporated down to dryness and the product was phthalimide XXII which melted at 235-236°C. The literature value for the melting point of phthalimide is given as 234°C.and 238°C.

The phthalic anhydride XXI (0.1 g.) was dissolved in a minimum amount of water and hydrolyzed with concentrated hydrochloric acid. The product, phthalic acid X, melted at 191-192.5°C. (sealed tube) which corresponded to the literature value for the sealed tube determination.

One part of phthalic anhydride XXI was mixed with 3 parts of phenol, moistened with concentrated sulfuric acid and heated until a brown solution formed. The reaction mixture was cooled, diluted with water and made alkaline with sodium hydroxide solution which caused the solution to give the well known test for phenolphthalein XXIV.

(ii) The black tar XII which remained in the distillation flask could not be distilled or recrystallized. It was quite soluble in ethyl alcohol and water. The tar was removed from the flask by dissolving it in ethyl alcohol and then the alcohol was distilled off. After an extraction with ether the black solid resembled pitch in its appearance. Sodium fusion tests showed that it contained both bromine and nitrogen.

A 10% solution of sodium hydroxide released pyridine from the tar as was easily detected by its odor. The black solid XII formed a precipitate with silver nitrate with an acidified solution of the tar. A complete analysis was run on the black pitch-like material.

Anal. Found: carbon 44.5, 44.3; hydrogen 3.55, 3.24; nitrogen (Dumas) 10.15, 10.10; bromine 32.8, 30.9.

From another run under similar conditions the black tar which remained in the distilling flask was not treated with any solvents, but was removed by heating the tar until it turned liquid and then poured off. This product when dissolved in water and acidified with nitric acid gave an immediate precipitate with a silver nitrate solution. This sample as the specimen above gave off the odor of pyridine when it was made alkaline with sodium hydroxide. It was also analyzed for all its elements. The yield was 4.8 g.

Anal. Found: carbon 48.00, 48.00; hydrogen 3.67, 3.74; nitrogen (Dumas) 5.71, 5.67; bromine 25.65, 24.77.

(iii) The liquid fraction which distilled at 33-40°C./0.3 mm. was never obtained in sufficient yield to be purified and analyzed. It XIII had a very sharp odor and was almost colorless. At atmospheric pressure when attempts were made to determine the boiling point by micro methods, the liquid turned dark brown and decomposed around 140-145°C.

(a) Sodium fusion tests showed the presence of bromine and nitrogen.

(b) An aqueous solution of XIII was acidic toward litmus.

(c) XIII did not liberate carbon dioxide from a saturated solution of sodium bicarbonate.

(d) XIII did not form a precipitate with 2,4-dinitrophenylhydrazine.

(e) XIII did not form a picrate or mercuric chloride derivative.

(f) With concentrated potassium hydroxide, ammonia gas was evolved.

(g) It did not give a precipitate with silver nitrate solution. The yield was too small to proceed further.

Reaction of 2-Bromo-2-nitro-1,3-indandione with Pyridine at Reflux Temperature of Pyridine

About 0.7 gram of 2-bromo-2-nitro-1,3-indandione VI was added to 10 ml. of pyridine in a 100 ml. flask. The mixture was kept at the reflux temperature for 2 hours.

During this time the yellow solution had turned a deep red. When the flask was cooled down in an ice bath some reddish brown crystals separated out. The reddish tint disappeared when the crystals were recrystallized from ethyl alcohol. The yellow crystals had a melting point 169-170°C. The yield was 0.45 gram. A mixed melting point with an authentic sample of 2-nitro-1,3-indandione showed no depression; melting point 169-170°C. with decomposition.

Hydrolysis of 2-Nitro-1,3-indandione Pyridinium Salt.

The 2-nitro-1,3-indandione pyridinium salt IX which was obtained from the reaction of 2-bromo-2-nitro-1,3-indandione with pyridine was treated with 10% sodium hydroxide solution. This hydrolysis gave pyridine and the sodium salt of 2-nitro-1,3-indandione XIV which could be isolated if so desired as a white crystalline compound. When the basic solution was acidified with concentrated hydrochloric acid the yellow 2-nitro-1,3-indandione V precipitated out. The absence of halogen was verified by a sodium fusion test. The yellow compound V had a melting point 113-114°C. The 2-nitro-1,3-indandione V was verified by two other derivatives. V formed a yellow crystalline solid with pyridine, 2-nitro-1,3-indandione pyridinium salt IX which melted at 168-169°C. with decomposition. An aqueous solution of V from the hydrolysis was brominated with bromine water and a white crystalline solid formed, 2-bromo-2-nitro-1,3-indandione VI, which had a melting point 110-111°C.

The pyridine which was split off during the hydrolysis was verified through its picrate, m.p. 163-164°C. A mixed melting point with an authentic sample of pyridine picrate gave no depression.

Preparation of 2-Nitro-1,3-indandione Pyridinium Salt from 2-Nitro-1,3-indandione and Pyridine

It was necessary to prepare an authentic sample of the pyridinium salt IX to compare it with the product from the main reaction IX to see whether the salts prepared in two different methods had any differences. To 5 ml. of dry pyridine was added 0.2 g. of 2-nitro-1,3-indandione. The solution was stirred and the yellow crystals formed even without cooling. The product 2-nitro-1,3-indandione pyridinium salt IX was recrystallized from ethyl alcohol. The yield was quantitative, m.p. 169-170°C. with decomposition.

Anal. Calcd. for $C_{14}H_{10}O_4N_2$: carbon 62.23; hydrogen 3.70; nitrogen 10.38.

Found: carbon 62.28, 62.39, 62.12, 62.02, 62.58; hydrogen 4.03, 3.85, 3.73, 3.79, 3.84; nitrogen (Dumas) 10.41, 10.29.

Molecular weight by Rast method 238; calcd. 270.

Reaction of 2-Bromo-2-nitro-1,3-indandione with Alpha, Beta, and Gamma Picoline

The picoline samples were freshly distilled prior to carrying out the reaction. To 2 ml. of alpha picoline was added 0.5 g. of 2-bromo-2-nitro-1,3-indandione; the solution turned yellow immediately and with vigorous stirring the main reaction product, 2-nitro-1,3-indandione-α-picolinium salt, XVI, formed within a few minutes as a beautifully yellow crystalline compound. The product XVI was recrystallized from ethyl alcohol. The yield was approximately 0.1 gram, m.p. 159.5-160.5°C. with decomposition. A mixed melting point with an authentic sample of 2-nitro-1,3-indandione-alpha-picolinium salt showed no depression.

With beta-picoline the same amount of material was used and the same procedure followed. The yellow crystalline product, 2-nitro-1,3-indandione-β picolinium salt XVIII was recrystallized from ethyl alcohol. The yield again was about 0.1 gram, m.p. 145-146°C. with decomposition. A mixed melting point with an authentic sample of 2-nitro-1,3-indandione-beta-picolinium salt showed no depression.

The product obtained when 2-bromo-2-nitro-1,3-indandione VI reacted with gamma picoline was the yellow crystalline compound 2-nitro-1,3-indandione-γ-picolinium salt XX. After recrystallization from ethyl alcohol the melting point was 172-173°C. with decomposition. The yield was about 0.1 g.

The reaction of β-picoline was considerably slower than the reactions of alpha or gamma picoline with 2-bromo-2-nitro-1,3-indandione. Considerable cooling was required before the yellow salt precipitated while in the other two instances the product formed at room temperature.

Hydrolysis of the Picolinium Salts

The 2-nitro-1,3-indandione picolinium salts (α, β and γ) prepared from 2-bromo-2-nitro-1,3-indandione and the respective picolines were subjected to hydrolysis in the same manner as the pyridinium salt IX with sodium hydroxide. The sodium salt of 2-nitro-1,3-indandione XIV was not isolated; the alkaline solution was acidified with concentrated hydrochloric acid. In each case the yellow crystals of 2-nitro-1,3-indandione V formed upon the addition of the acid. The 2-nitro-1,3-indandione from the alpha and gamma picolinium salts melted at 115-116°C.; the melting point of the 2-nitro-1,3-indandione V from the hydrolysis of the beta salt was 118-119°C.

Preparation of 2-Nitro-1,3-indandione Picolinium Salts

To 5 ml. of freshly distilled warm picoline, alpha, beta and gamma respectively, was added 0.5 g. of

2-nitro-1,3-indandione. The products in each case were yellow crystalline solids which were recrystallized from ethyl alcohol. The melting points were observed: 2-nitro-1,3-indandione-alpha-picolinium salt 160-161°C. with decomposition; 2-nitro-1,3-indandione-beta-picolinium salt 145-146°C. with decomposition; 2-nitro-1,3-indandione-gamma-picolinium salt 172-173°C. with decomposition.

Isolation of Phthalic Acid from the Reaction of 2-Bromo-2-nitro-1,3-indandione with Pyridine

The reaction between 2-bromo-2-nitro-1,3-indandione VI with pyridine was carried out many times and the precipitate which formed consisted mainly of 2-nitro-1,3-indandione pyridinium salt IX. This crude product after having been investigated was merely saved in future reactions. After the crude product had accumulated to about 10 grams, it was extracted with ether. After the ether was distilled off, some white crystalline material, phthalic acid X, remained which melted at 195-196°C. (crude). The crude product was heated in a sublimation apparatus above 200°C. which transformed the phthalic acid X into phthalic anhydride XXI. The melting point of the phthalic anhydride XXI was 128-129°C. The phthalic anhydride was verified by transforming it into phenolphthalein XXIV by heating it with sulfuric acid and phenol.

Investigation of the Purity of 2-Bromo-2-nitro-1,3-indandione

About 0.5 gram of 2-bromo-2-nitro-1,3-indandione VI was heated in a sublimation apparatus under reduced pressure above 200°C. It was observed that when the 2-bromo-2-nitro-1,3-indandione melted it turned into a light green liquid, but no phthalic anhydride formed on the cold finger. This same phenomenon, the formation of the green liquid, was observed when the 2-bromo-2-nitro-1,3-indandione VI underwent combustion in the Pregl apparatus.

As a further check on VI it was treated with phenol and sulfuric acid, but it did not give the pink color of phenolphthalein when sodium hydroxide was added to the cooled and diluted solution.

Bromination of Pyridine

0.1 M bromine (15.98 g) was added by means of a dropping funnel over a period of 35 minutes to 0.1 M of pyridine (7.9 g.) which was dissolved in 25 ml. of acetonitrile. The reaction flask was a 100 ml. round bottom flask equipped with a reflux condenser and a dropping funnel. During the addition of bromine the solution turned deep red. When all the bromine had been added, the mixture was heated very gently with a Glascol-Mantel; the reaction became so strongly exothermic that it had to be cooled with an ice bath. The mixture turned into a dark brown viscous liquid which was poured into 150 ml. of water. Immediately orange-red crystals of pyridine perbromide formed in the solution. The pyridine perbromide XXV could not be recrystallized. The yield was 8.0 g, 33% of the theoretical, m.p. 61-63°C. Pyridine perbromide, being unstable, decomposed after 36 hours with an evolution of bromine and turned into a hard dark brown solid mass. The pyridine perbromide $C_5H_5NBr_2$ formed a picrate with picric acid, m.p. 163-164°C. In the pyridine picrate the absence of halogen was shown by sodium fusions. No depression was observed with an authentic sample of pyridine picrate.

Preparation of Pyridine Perbromide

0.1 M of freshly distilled pyridine (7.9 g.) was dissolved in 25 ml. of redistilled carbon tetrachloride. To this solution 0.1 M. of bromine (15.9 g.) was added drop by drop; during the addition of bromine only a few degrees rise in temperature was noted. The orange-red pyridine perbromide XXV precipitated out when all the bromine had been added and it was washed with carbon tetrachloride and dried in a desiccator. The yield was 10 g., 40% of the theoretical, m.p. 63-64°C. A mixed melting point was taken with the pyridine perbromide prepared in the acetonitrile solvent, m.p. 62-63°C. After about 20 hours the perbromide decomposed with the evolution of bromine into a hard brown solid.

Reaction of Pyridine Perbromide with Aniline, Ortho-toluidine and Cyclohexyl Amine

To 3 g. of freshly distilled aniline was added an acetonitrile solution of pyridine perbromide until the deep red crystals appeared. The reaction gave off considerable heat and the flask was cooled with running water. The product, aniline hydrobromide, XXVI which formed was recrystallized twice from acetic acid and from this treatment the crystals had a pinkish red color; the yield was 2.0 g. The color disappeared around 200°C. and gradual melting continued to nearly 260°C. This same behavior in melting was observed with a pure white sample of aniline hydrobromide, although the melting point is given as 285°C. in many melting point tables. The red product was analyzed for its elements.

[*]*Anal*. Calcd. for $C_4H_8N_1Br_1$: carbon 41.25; hydrogen 4.59; nitrogen 8.04; bromine 45.97.

Found: carbon 41.03, 41.28; hydrogen 4.43, 4.38; nitrogen 8.24; bromine 45.37, 45.77.

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The aniline hydrobromide XXVI formed in the above reaction was red while the aniline hydrobromide prepared from aniline and hydrobromic acid is colorless. The pH of the two solutions of aniline hydrobromide was compared; the white aniline hydrobromide and the red specimen both had a pH of 2.7 in a 4.3 M solution. The colored XXVI was treated with nitrous acid at 0°C. and when the diazotized solution was added to a sodium hydroxide solution of beta-napthol a deep orange colored dye was observed.

Continued recrystallizations from acetic acid with Norite gave a colorless product, aniline hydrobromide.

0.1 g. of aniline hydrobromide XXVI was dissolved in ethyl alcohol to which was added 0.2 g. of 2-nitro-1,3-indandione. The product was the anilinium salt of 2-nitro-1,3-indandione which after recrystallization from ethyl alcohol melted at 208-210°C. An authentic sample of the same salt prepared by adding 2-nitro-1,3-indandione to aniline had a melting point of 208-210°C. A mixed melting point of the two anilinium salts showed no depression, m.p. 208-210°C.

A solution of pyridine perbromide was added to 3 g. of ortho-toluidine; the addition was continued until the dark precipitate had formed. Repeated recrystallizations from acetic acid with Norite gave a colorless product, ortho-toluidine hydrobromide XXVIII, m.p. 203-204°C.; the yield was 0.65 g. The melting point was compared with a sample of the salt prepared by the reaction of hydrobromic acid with ortho-toluidine. Both salts and a mixed melting point had a value of 203-204°C. Approximately 0.1 g. of ortho-toluidine hydrobromide XXVIII was dissolved in ethyl alcohol and treated with 0.2 g. of 2-nitro-1,3-indandione. The yellow salt had a melting point of 210-211°C. An authentic sample of the same product was prepared by reacting 2-nitro-1,3-indandione with ortho-toluidine, m.p. 210-211°C.; no depression was observed in a mixed melting point determination of the two samples.

Finally the reaction was repeated using a non-aromatic reactant, cyclohexyl amine. The pyridine perbromide solution was added to 3 g. of cyclohexyl amine until the contents of the flask turned solid. The product, cyclohexyl amine hydrobromide XXX was recrystallized from acetic acid, m.p. 205-207°C.; the yield was 3.0 g. This reaction mixture did not become as dark as the two previous reactions with aromatic amines. The reaction of hydrobromic acid with cyclohexyl amine gave a salt which melted at 205-207°C.; a mixed melting point showed no depression. The 2-nitro-1,3-indandione salt prepared from the reaction product, cyclohexyl amine hydrobromide XXX and from cyclohexyl amine both melted at 209-210°C.

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SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

1. Previously it was observed that a crystalline product was formed when 2-bromo-2-nitro-1,3-indandione was allowed to react with pyridine. This material was identified as the pyridinium salt of 2-nitro-1,3-indandione; this same product formed at room temperature and also at the reflux temperature of pyridine. A thorough study of the reaction at room temperature showed that phthalic acid, pyridine hydrobromide, a polymer and possibly bromonitromethane were also products of the same reaction. This investigation has given additional support to the claim that the halogen in 2-bromo-2-nitro-1,3-indandione reacts as a positive bromine atom.

2. The reaction was extended to alpha, beta and gamma picoline; the main reaction product in each instance was the picolinium salt of 2-nitro-1,3-indandione.

3. From the bromination of 2-nitro-1,3-indandione a by-product, phthalic acid, was isolated which was previously unnoticed.

4. The modern views of electronic theory were applied to 2-nitro-1,3-indandione. Its structure in aqueous solution was shown to be largely the nitro ketone and not the aci- form as was previously supposed.

The aci- form of 2-nitro-1,3-indandione was isolated and it was shown to give a test with ferric chloride solution unlike the normal keto form.

5. The action of bromine on pyridine in acetonitrile was found to give pyridine perbromide.

6. An investigation of the reaction of pyridine perbromide with aniline led to a new reaction. The amine hydrobromide is produced when pyridine perbromide reacts with an amine. The reaction is general and can be used for aliphatic as well as aromatic amines.

7. It was found that pyridine perbromide, a very unstable substance, could be preserved for a week and longer if it were stored under water at 0°C. Since pyridine perbromide is an important chemical for preparing some bromo pyridines and had to be prepared freshly for each reaction, this finding should facilitate these brominations.

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