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THE REDUCTION OF AROMATIC NITRO COMPOUNDS
WITH ANHYDROUS STANNOUS CHLORIDE

By

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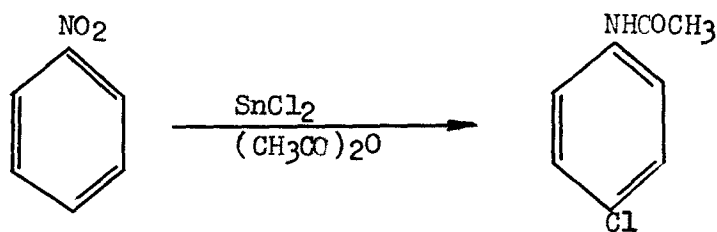
NEWARK COLLEGE OF ENGINEERING

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I - INTRODUCTION

With the publication of a method for the preparation of anhydrous stannous chloride (1), T. E. de Kiewiet and H. Stephen were prompted to investigate its use in the reduction of aromatic nitro compounds under anhydrous conditions. In a paper entitled "A New Method of Reducing Aromatic Nitro Compounds" (2), reporting the results of this investigation, they claimed simultaneous reduction, acetylation, and also chlorination in the position para to that of the original nitro group.



In experiments using para substituted nitro compounds, they found that no chlorination took place except in the case of para-chloronitrobenzene, which, if hydrochloric acid were present during the reaction, gave 2, 4-dichloroacetanilide. In the absence of hydrochloric acid, para-chloroacetanilide was formed.

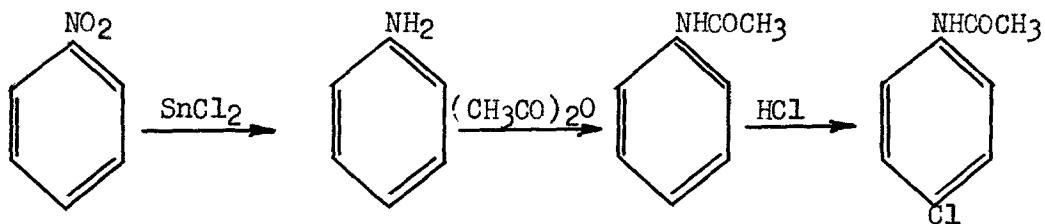
Careful following of their directions for the reaction with nitrobenzene (simplest of the aromatic nitro compounds) failed to confirm their claim of almost theoretical yields, although the experiment did prove their claim that the only isolated product of

the reaction was para-chloroacetanilide in almost pure form (melting point 173-174°C). Repeated experiments following their directions resulted in a yield of approximately ten percent of the theoretical yield.

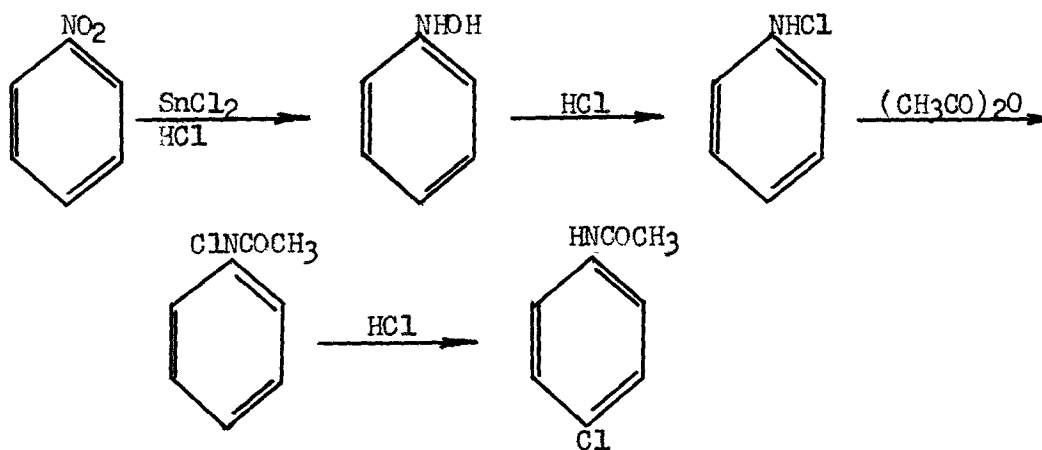
As a result of the inability to reproduce the results which these authors reported, it was decided to investigate this reaction with a view to determining: the conditions under which the best yield could be obtained; the effect of blocking the position para to the nitro group; the effect of other groups on the benzene ring, in other than the position para to the nitro group; and the effect of two nitro groups on the ring.

II - EXPERIMENTAL

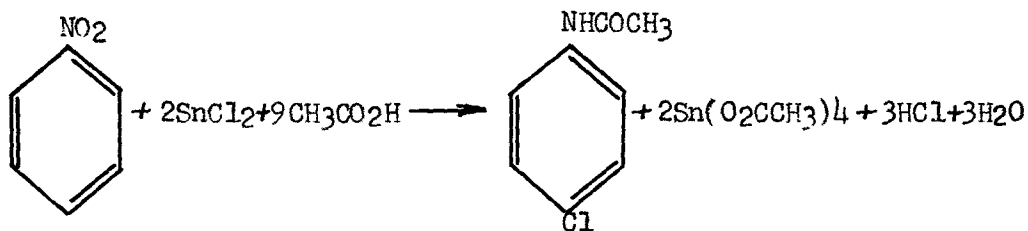
The first experiments were run to determine the conditions under which the best overall yield could be obtained for the reaction with nitrobenzene. This was done by varying both the concentrations of the reactants and the length of time the reaction mixture was heated at reflux. The theoretical mechanism of the reaction could be by the route:



De Kiewiet and Stephen found that the product of the reaction for β -phenylhydroxylamine and the product of the reaction for nitrobenzene, using the same method, was para-chloronitrobenzene; they suggested that β -phenylhydroxylamine might be an intermediate product in the reduction of nitrobenzene. The theoretical mechanism of the reaction, if this were so, could be by the route:



The reaction with nitrobenzene might be expressed by the equation:



This would indicate a mole proportion of nitrobenzene to stannous chloride to acetic acid of 1:2:9, or based on hydrated stannous chloride and acetic anhydride of 1:2:4.5. The proportion of re-

actants recommended by de Kiewiet and Stephen was 1:3:9. If the theoretical equation is assumed to be correct, this is a fifty percent excess of reducing agent and a thirty-three percent excess of acetic acid. The yield obtained for nitrobenzene, using this mole proportion of reactants and a reflux time of thirty minutes, was approximately ten percent of the theoretical yield of para-chloroacetanilide.

The mole proportion of reactants in the next experiment tried was 1:4:16. This was a one hundred percent excess of reducing agent, a sixty-six percent excess of acetic acid, and acetic anhydride in excess of that required to dehydrate the stannous chloride. In this experiment all of the stannous chloride did not go into solution on thirty minutes of reflux, and on cooling the reaction mixture, large quantities of anhydrous stannous chloride crystallized from the solution. The yield of para-chloroacetanilide was nil.

In the final experiment of this series, that found to give the highest yield, the mole proportion of reactants was 1:3:12. This was a fifty percent excess of reducing agent, a thirty-three percent excess of acetic acid, and a one hundred percent excess of acetic anhydride beyond that needed for dehydration of the stannous chloride. The yield of para-chloroacetanilide, using this proportion of reactants and a reflux time of thirty minutes, was twenty-two percent of the theoretical yield.

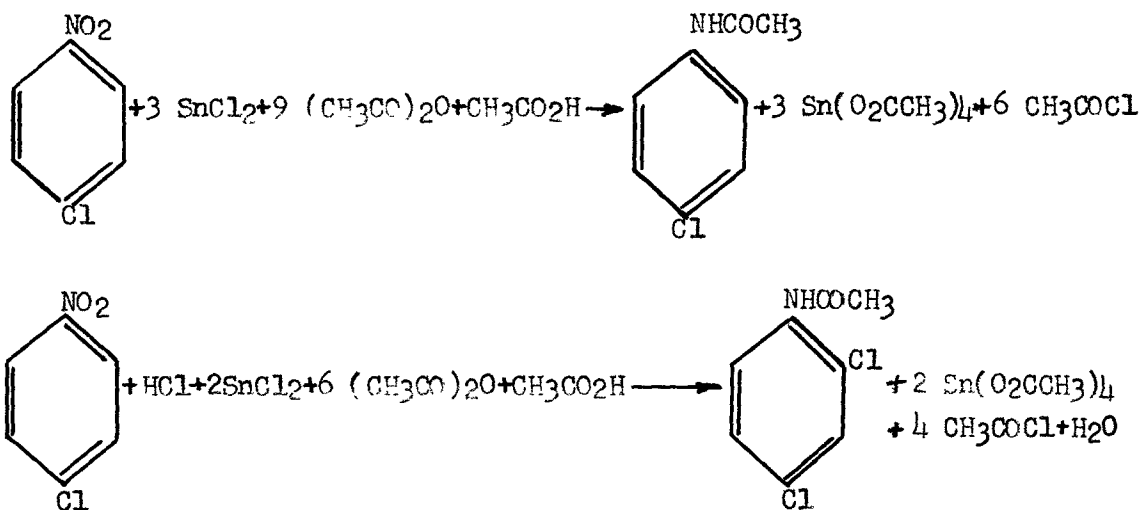
The effect of time was then determined by running a series of experiments in which the reflux time was varied from two hours to just long enough to effect complete solution of the reactants. De Kiewiet and Stephen recommended a reflux time of thirty minutes for the reaction with nitrobenzene. The mole proportion of the reactants in this series of experiments was 1:3:12, the proportion which was found to give the best yield for thirty minutes of reflux in the preceding experiments. In the first experiment of this series, the reflux time was two hours. The color of the reaction mixture after this period of time was almost black, and the only material which could be isolated was a tar. The time of reflux in the next experiment was sixty minutes, and the only material separated was a black oily liquid. Since the color of the reaction mixture became darker with an increase in reflux time, it was decided to heat only long enough to effect complete solution of the reactants. This was done in the next experiment, and a clear solution was obtained after about fifteen minutes of reflux. The color of the reaction mixture and the isolated para-chloroacetanilide was pale yellow. The yield of para-chloroacetanilide was thirty-seven percent of the theoretical yield, and the melting point was 176-177°C.

The complete method giving the best yield for the reaction with nitrobenzene was as follows:

Finely ground crystalline $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.3 moles) was treated with acetic anhydride (1.2 moles) in a 500 ml. round bottom flask. After dehydration was complete, the flask was cooled to approximately 50°C , and 0.1 mole of nitrobenzene was slowly added with constant mixing. When the addition was complete, the flask was attached to a reflux condenser and refluxed until the solution went clear (about fifteen minutes). As soon as a clear solution was obtained, the flask was removed and cooled in cold running water. The unreacted acetic acid and acetic anhydride were removed by distillation under reduced pressure, at as low a temperature as possible. The residue was treated with just enough hot water to effect solution, and filtered while hot. On cooling, para-chloroacetanilide separated in almost pure form (melting point $176-177^\circ\text{C}$). The crystalline product was filtered and washed with several small portions of cold water.

III - EXPERIMENTAL

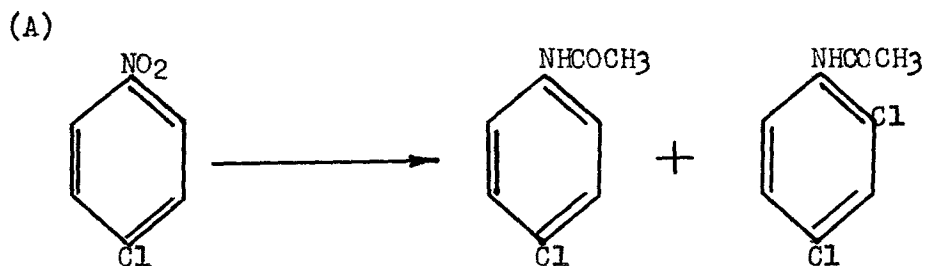
De Kiewiet and Stephen reported that monochlorination took place in the position para to the original nitro group when this position was unoccupied. The only exception they found was in the case of the reaction with para-chloronitrobenzene, which, if hydrochloric acid were present, yielded 2,4 - dichloroacetanilide. In the absence of hydrochloric acid, the only product was para-chloroacetanilide. These two reactions might be expressed as:



The reaction with para-chloronitrobenzene was tried and found to yield a mixture of the mono- and di-chloroacetanilide.

In order to find whether this was an isolated example, a series of experiments were run in which the position para to the nitro group was occupied. In most cases, the products were isolated in almost pure form as indicated by their melting points. The product of the reaction was identified by the melting point.

The experiments tried were as follows:

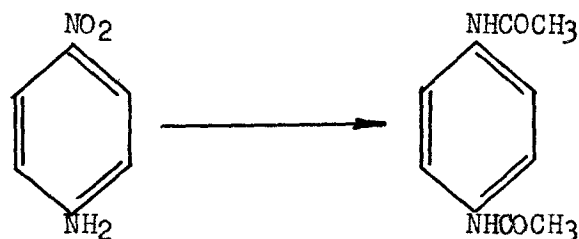


Finely ground $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.3 mole) was treated with

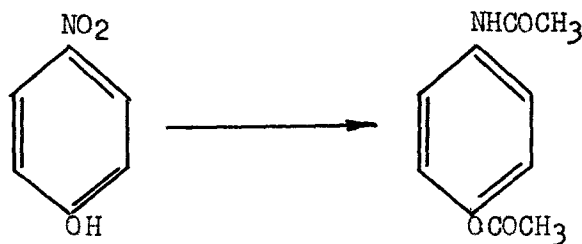
acetic anhydride (1.2 moles). When the dehydration was complete the mixture was cooled to approximately 50°C and 0.1 mole of para-chloronitrobenzene was slowly added. The mixture was heated to boiling and allowed to reflux for about two minutes until the solution went clear. The flask was cooled, and the acetic acid-acetic anhydride removed by distillation at twenty millimeters pressure. The residue was treated with 150 ml. of water and heated until clear. On standing over night in the refrigerator, crystallization took place. The crystals were filtered and washed with cold water, then air dried at 105°C. The weight of the product was 14.5 grams, and the melting range was 130-155°C. A portion of the crude product was dissolved in hot glacial acetic acid, filtered, and diluted with an equal quantity of water. On cooling crystals were formed, which were filtered, washed with cold water, and air dried. The product was identified as para-chloroacetanilide (melting point 177°C).

A second portion of the crude product was repeatedly recrystallized from water until a very small amount of a white solid was obtained, which was identified as 2,4-dichloroacetanilide (melting point 144-145°C).

(B)



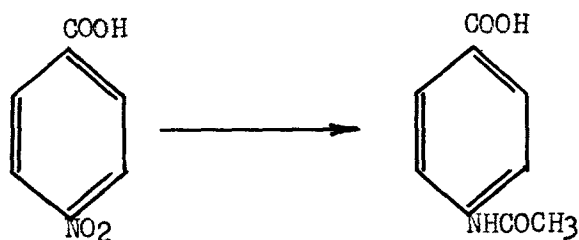
The reaction mixture, (0.3 mole $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$; 1.2 moles acetic anhydride), was prepared as before. Para-nitroaniline (0.1 mole) was added, heated to boiling, and refluxed for five minutes until the solution became clear. The acetic acid-acetic anhydride was removed by distillation at reduced pressure. After about three quarters of the acetic acid had been distilled, crystals began to form. When the residue froze to a solid mass, the heat was removed. Two hundred milliliters of water were added and the crystals filtered, washed, and dried. The product consisted of 16.8 grams of N,N'-diacetyl-paraphenylene diamine (melting point $304-305^\circ\text{C}$).



The reaction mixture was prepared as before, and 0.1 mole of para-nitrophenol was added. The mixture was heated at reflux until a clear solution was obtained (about 10 minutes). Approximately one-half the volume of liquid had been distilled when crystallization began to take place. The distillation was stopped and the flask placed in the refrigerator over night. The next day there was a mass of crystals which were filtered without vacuum. The crystals were transferred to a beaker and 50 ml. of

hot water added. On cooling in a dry ice-acetone bath, there was a separation of crystals which were filtered, washed with cold water, and dried at 105°C. The product was 8.3 grams of para-acetamidophenyl acetate (melting point 151-152°C).

(D)



Para-nitrobenzoic acid (0.1 mole) was added to the reaction mixture. The mixture was refluxed for about five minutes until clear. The acetic acid-acetic anhydride was removed by distillation at reduced pressure, and the residue dissolved in 200 ml. of hot water. On cooling, 4.1 grams of para-acetamido benzoic acid separated. The melting point of the crude product was 248-249°C, and that of the product recrystallized from water 250-251°C.

(E)



One tenth mole of para-nitrotoluene was gradually added to the reaction mixture. The mixture was heated to boiling and refluxed for ten minutes until the solution went clear. The acetic acid-acetic anhydride was removed by distillation at reduced

pressure and the residue treated with 200 ml. of water. This solution was heated until clear, and filtered while hot. Cooling the solution in an ice bath caused an oil to settle, which was crystallized by scratching with a glass rod. The product consisted of 10.5 grams of acet-para-toluidide (melting point 145-146°C).

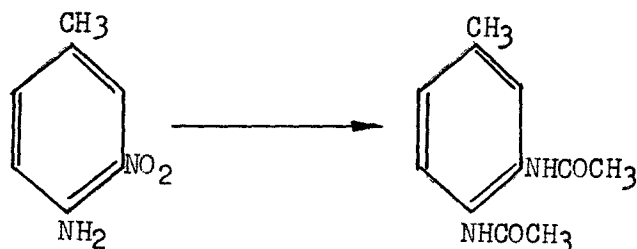
For this series of experiments, where the position para to the nitro group was occupied, the only case where chlorination was found to take place was in the experiment with para-chloro-nitrobenzene. This experiment yielded a mixture of 2,4-dichloro-acetanilide and para-chloroacetanilide.

The yields of the reaction ranged from 23% to 89% of the theoretical yields. The yield of 89%, obtained in the experiment with para-nitroaniline, was probably due to the very low solubility of the N,N'-diacetyl-para-phenylenediamine in the solvent. In the first experiment with para-nitrophenol, no solid product could be isolated. In this experiment, the distillation for the removal of the acetic acid-acetic anhydride was continued until no more liquid distilled over, even though the head temperature rose sharply above the boiling point of acetic anhydride at the existing pressure. The procedure was modified, and the product para-acetamino phenyl acetate was obtained at 43% of the theoretical yield.

IV - EXPERIMENTAL

De Kiewiet and Stephen stated that mono-chlorination took place para to the original nitro group in all cases where this position was unoccupied. The only exceptions which they reported was in the case of ortho-nitrophenol and certain of its derivatives. All of their work however, with the exception of 2-nitro-4-methyl-phenol (an ortho-nitrophenol derivative), was done on nitro compounds containing only one group on the ring in addition to the nitro group. In order to determine whether mono-chlorination would take place when the para position were unoccupied, and there was more than one other group on the ring in addition to the nitro group, the following experiments were run:

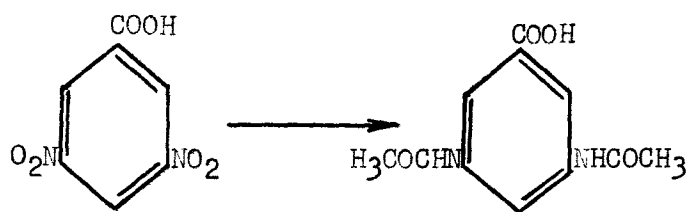
(F)



The reaction mixture was prepared, and 17.9 grams of 3-nitro-4-amino-toluene was added. Upon the addition of the nitro compound, the temperature rose sharply, and it was necessary to cool the flask in water after each portion of the nitro compound was added. After the addition was complete, the mixture was care-

fully heated and refluxed until clear. The acetic acid-acetic anhydride was removed under reduced pressure, and 250 ml. of water added to the residue, which was an oily liquid. Upon the addition of water, there was a separation of crystals which were filtered, washed with cold water, and dried at 105°C. The product was N,N'-diacetyl-3,4-diamino toluene (melting point 209.5-210°C).

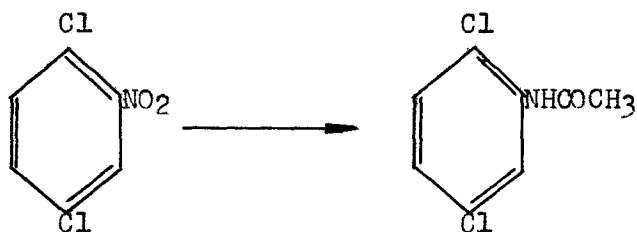
(G)



Ten and six-tenths grams of 3,5-dinitrobenzoic acid were added to the reaction mixture, and the mixture refluxed until a clear solution was obtained. The acetic acid-acetic anhydride was removed by distillation at reduced pressure, and 100 ml. of water added to the residue. Upon the addition of water there was a separation of crystals which were filtered, washed with cold water, and dried at 105°C. The melting point of this crude product was 292-295°C. A portion recrystallized from water had a melting point above 300°C. A sodium fusion was run on the recrystallized material, and the test for chlorine was negative. It was suspected that the product was the corresponding N,N'-diacetyl derivative, and a neutral equivalent was run. The recrystallized material (0.2553 grams) was dissolved in approximately 500 ml. of

hot water, and titrated to the phenolphthalein end point with 9.20 ml. of 0.1187N KOH. The neutral equivalent found was 234 (theoretical value for N,N'-diacetyl-3, 5-diamino benzoic acid is 236).

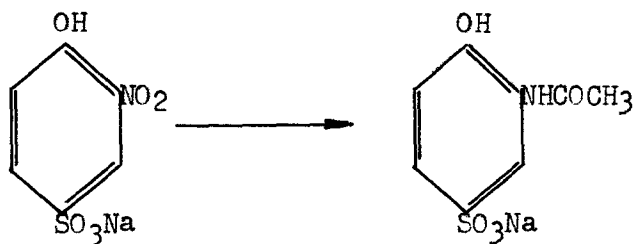
(H)



The 2,5-dichloronitrobenzene used in this experiment was prepared by the nitration of para-dichlorobenzene, following the method of H. J. Page and B. R. Heasman (3).

The method used in this experiment was the same as for the previous one, and the product was identified as 2,5-dichloroacetanilide by its melting point of 132°C.

(I)

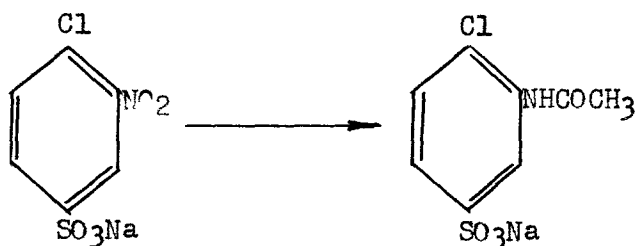


One-tenth mole of the nitro compound was added to the reaction mixture which was prepared as previously described. The solution was slowly heated, but when the temperature reached

approximately 100°C the temperature rose sharply and the solution began to boil vigorously. Heating was continued until the reaction was apparently complete, but the solution did not go completely clear. The flask was cooled, and a small amount of solid was separated. This material was soluble in water, and appeared to be common salt which had contaminated the sodium sulfonate. The filtrate was returned to the flask, and the acetic acid-acetic anhydride removed by distillation at reduced pressure. The residue was dissolved in 150 ml. of hot water, and the solution cooled in an ice bath. There was no crystal formation, so the volume of liquid was reduced by one-half and sodium chloride added to salt out the product. After standing in the refrigerator for one week crystals formed, which were separated and dried. The solid product had no melting point, did not fuse, and left a residue upon ignition which contained sodium. A test for halogens, after a sodium fusion, gave only a slight turbidity which was probably due to contamination of the material with sodium chloride. A water solution of the compound was acid, and decolorized potassium permanganate solution and bromine water. It was suspected that the product was the corresponding acetamido-hydroxy-benzene sodium sulfonate, and since the melting point of a derivative could not be found in the literature, the percentage of nitrogen was determined by the Dumas method. The sample used for this determination was repeatedly recrystallized from a minimum amount of water. The percentage of nitrogen found was 5.48%; the theoretical value for 3-acetamido-

4-hydroxy-benzene sodium sulfonate is 5.53%.

(J)



This experiment was done in the same manner as the previous one. In this case however, it was not necessary to salt out the reaction product. The product had no melting point, and left a residue on ignition which contained sodium. It was suspected that the product was the corresponding acetamido-chloro-benzene sodium sulfonate, and since the melting point of a suitable derivative could not be found in the literature, the percentage of nitrogen was determined by the Dumas method. The percentage of nitrogen found was 4.99%; the theoretical value for 3-acetamido-4-chloro-benzene sodium sulfonate is 5.15%.

In none of the preceding cases did mono-chlorination take place, despite the fact that the position para to the nitro group was always unoccupied. In the reaction with 3-nitro-4-hydroxy-benzene sodium sulfonate the hydroxyl group was not acetylated during the reaction, although there was sufficient acetic anhydride present to bring about this reaction. This was in agreement with the findings of de Kiewiet and Stephen in regard

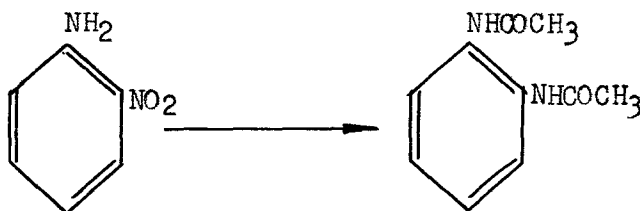
to derivatives of ortho-nitrophenol.

V - EXPERIMENTAL

In order to determine whether chlorination would take place when the positions para to each of two nitro groups were unoccupied, the experiment was tried using meta-dinitro-benzene. No solid product of the reaction could be isolated by crystallization from a water solution of the residue, by extraction with hot benzene, extraction with ethyl ether, or by steam distillation from a basic solution. The experiment was repeated with the same result. In the working up of the reaction mixture all of the materials went into solution, but the solution quickly turned from a light yellow to a dark brown color, possibly indicating decomposition of the products.

VI - EXPERIMENTAL

(K)



The final experiment was with ortho-nitroaniline. Addition of the nitro compound to the reaction mixture resulted in the evolution of much heat. No outside heating was necessary

to bring the solution to reflux temperature, but it was found necessary to cool the flask in order to keep the reaction under control. After the acetic acid-acetic anhydride had been removed by distillation, the residue was dissolved in 100 ml. of hot water. On cooling of the solution there was no crystal formation. The solution was made basic with potassium hydroxide, and extracted with ethyl ether. On evaporation of the ether, a dark orange solid was obtained (melting point 173-179°C). A test for halogens after sodium fusion was negative. The material was repeatedly recrystallized from water, and pale yellow crystals were obtained which were identified as N,N'-diacetyl-orthophenylene-diamine (melting point 184-185°C).

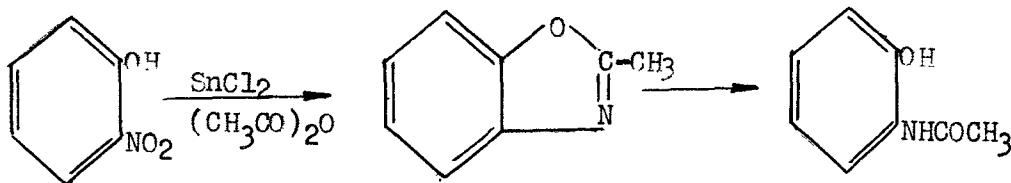
VII - CONCLUSION

The purpose of this work was to attempt to duplicate the findings of de Kiewiet and Stephen, especially in regard to the yields claimed by these authors, and to test the method on other aromatic nitro compounds. Use of their method, in the case of nitrobenzene, resulted in a yield of approximately ten percent, as opposed to their claim of almost theoretical yield for this reaction. The presence of acetic anhydride during the reaction, as well as a minimum of heating, was found to increase the yield, in the case of nitrobenzene, to approximately forty percent.

Experiments were carried out on a number of other

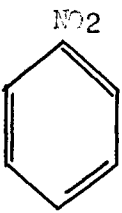
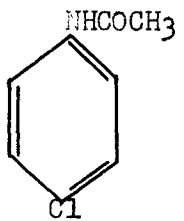
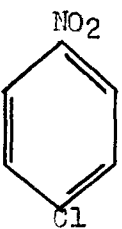
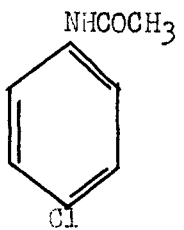
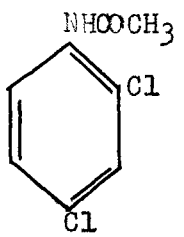
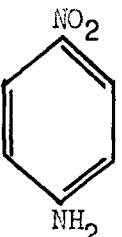
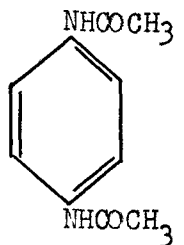
aromatic nitro compounds using the proportion of reactants found to give the best yield in the case of nitrobenzene. In the experiments tried where the position para to the nitro group was occupied, the findings of de Kiewiet and Stephen were confirmed, and mono-chlorination took place only in the case of the reaction with para-chloronitrobenzene. These authors also claimed however, that in all cases (with the exception of ortho-nitro phenol and its derivatives) when the position para to the nitro group was unoccupied, mono-chlorination of the ring took place. The experiments described in this paper show that this is not true where there is more than one other group on the ring in addition to the nitro group.

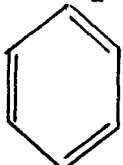
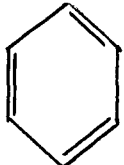
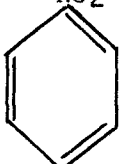
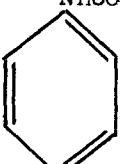
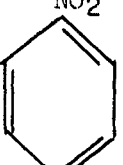

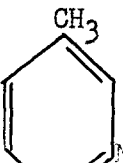
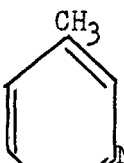
In the reaction with 3-nitro-4-hydroxy-benzene sodium sulfonate, acetylation of the hydroxyl group did not take place, although there was sufficient acetic anhydride present to bring about this reaction. It is possible that the α -methylbenzoxazoles are intermediate products in the reduction of ortho-nitrophenolic compounds as suggested by de Kiewiet and Stephen.

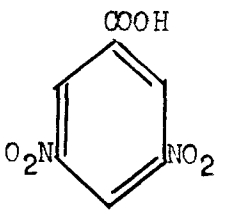
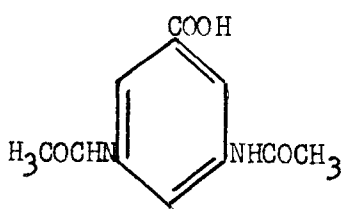
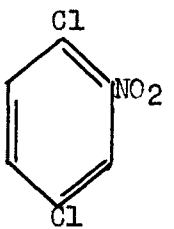
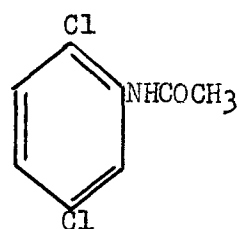
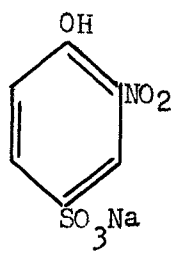
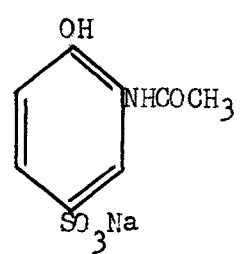
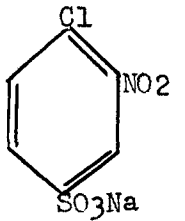
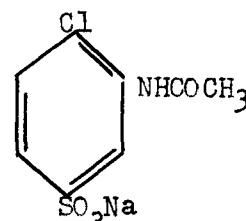


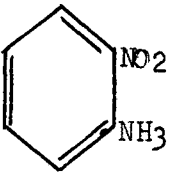
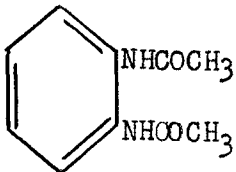
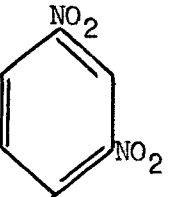
The lowest yield obtained was nineteen percent of the theoretical yield in the reaction with 2, 5-dichloronitrobenzene. The highest yield was eighty-nine percent obtained in the reaction with para-nitroaniline. The average yield was approximately fifty percent.

The following table is a summary of the reactions tried, and indicates the product isolated and the yields obtained:

Exp. No.	Nitro Compound Used	Its Wt. Grams	Product	Its Wt. Grams	Melting Pt. (°C)	Yield %
1		12.3		6.2	176-7	36.6
2		15.8	 + 	14.5	177	144-5
3		13.6		16.8	304-5	89

Exp. No.	Nitro Compound Used	Its Wt. Grams	Product	Its Wt. Grams	Melting Pt. (°C)	Yield %
4	NO_2  OH	13.9	NHCOCH_3  OCOCH_3	8.3	151-2	43
5	NO_2  COOH	16.7	NHCOCH_3  COOH	4.1	250-1	23
6	NO_2  CH_3	13.7	NHCOCH_3  CH_3	10.5	145-6	70
7	CH_3  NO_2 NH_2	17.9	CH_3  NHCOCH_3	6.3	209.5-10	28

Exp. No.	Nitro Compound Used	Its Wt. Grams	Product	Its Wt. Grams	Melting Pt. (°C)	Yield %
8		10.6		6.8	above 300	58
9		19.2		3.9	132	19
10		24.8		10.3		34
11		21.2		12.5		53

Exp. No.	Nitro Compound Used	Its Wt. Grams	Product	Its Wt. Grams	Melting Pt. (°C)	Yield %
12		13.8		10.2	184-5	53
13		8.4	No product isolated			Nil

VIII - LITERATURE CITED

- (1) Stephen, H., J.C.S. 1930, 2786
- (2) De Kiewiet, T.E., and Stephen, H., J.C.S. 1931, 82
- (3) Page, H.J., and Heasman, B.R., J.C.S. 1923, 3247