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The reactions of aliphatic nitroso compounds.

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Thesis

THE REACTIONS OF ALIPHATIC NITROSO COMPOUNDS

by

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INTRODUCTION

This research was undertaken to investigate the action of various oxidizing agents, both organic and inorganic, on two typical aliphatic nitroso compounds. The first aim was to transform the nitroso compounds into their respective nitro compounds. It has been reported in Houben-Weyl[6] that various reagents are capable of completing this reaction including chromic acid in acetic acid, 10% hydrogen peroxide, and potassium ferricyanide depending upon the starting product. This investigation has tested the action of benzoyl peroxide, acetyl peroxide, urea peroxide, nitric acid, potassium ferricyanide, and 30% hydrogen peroxide.

As a typical C-nitroso compound, propyl pseudonitrole ($(CH_3)_2C(NO)NO_2$) was chosen. This compound in the solid state is in the form of the dimer, but in solution it breaks down into the monomer forming a blue solution. This characteristic color was utilized in the experimentation as an indication of a reaction. The disappearing or fading of the color could be taken as good evidence that some reaction had occurred. Separation of the 2,2-dinitro compound from the pseudonitrole could be effected by steam distillation the former being volatile with steam.

N-Nitrosodimethylamine ($(CH_3)_2NNO$) was chosen as a typical N-nitroso compound. In this case there was no

characteristic color to aid in the detection of a reaction. Due to the fact that the N-nitro compound sublimes readily it was felt that a separation could be caused in this manner.

During the investigation two interesting preparations of 2,3-dinitro-2,3-dimethyl butane were found. In the first 2-nitropropane is dissolved in a slight excess of aqueous alkali (29%). Sodium nitrite is then added to this solution. The resulting mixture is taken to the phenolphthalein end point by adding sulfuric acid. Finally a mixture of sulfuric acid and hydrogen peroxide is added to the solution. The dinitro compound separates and may be filtered. Several experiments were carried out to determine the reacting species in this reaction. A thorough investigation proved to be beyond the scope of this research.

The second preparation is brought about by adding ethylchlorocarbonate to a basic solution of 2-nitropropane. An experiment was carried out to determine the function of the ethylchlorocarbonate.

PREPARATION OF PROPYL PSEUDONITROLE [5]

Approximately 0.07 mole of 2-nitro propane (6 grams) was dissolved in 15cc. of 29% aqueous potassium hydroxide (0.1 mole) by shaking in a heavy walled glass bottle. The temperature was kept at a minimum by adding cracked ice during the solution process. The solution was then transferred to a three necked flask containing an aqueous solution containing 0.072 mole of sodium nitrite (5 grams). The flask was equipped with a dropping funnel, an efficient stirrer, and a thermometer. The temperature was lowered to 0° C. by adding cracked ice and by surrounding the flask with an ice bath. Sulfuric acid (3N) was added dropwise; the temperature of the reaction mixture being kept between -5° and +5° C. by adding cracked ice as necessary.

As the reaction mixture became acidic the color changed from a straw-yellow to blue and a solid began separating out. Acid was added until further addition did not precipitate any more solid. The solid was then filtered through a Buchner funnel and dried. It had a melting point of 74° C. with decomposition. The melting point of propyl pseudonitrole reported in the literature is 75° C. with decomposition. The yield amounted to 4 grams or approximately 50 % of the theoretical.

SOLUBILITY OF PROPYL PSEUDONITROLE

Due to the fact that propyl pseudonitrole is only very slightly soluble in water an organic solvent had to be used. The solvents tested and the results are as follows:

1. slightly soluble in ether giving blue color
2. soluble in carbon tetrachloride giving blue color
3. soluble in glacial acetic acid giving blue color
4. slightly soluble in ligroin giving blue color
5. soluble in chloroform giving blue color
6. soluble in ethyl acetate giving blue color
7. soluble in dioxan giving blue color

It was found in all cases that shaking was necessary to dissolve the nitrole and that in no case did it give a blue color immediately. With dioxan, apparently the best solvent employed, it was a matter of 10 seconds before the characteristic blue was noted to any extent.

OXIDATION WITH NITRIC ACID - TRIAL 1

A saturated solution of the pseudonitrole in 20cc. of glacial acetic acid was prepared. This was added dropwise to about 20cc. of fuming nitric acid warmed in a steam bath. Brown fumes were noted escaping from the reaction mixture. It was heated until no more brown fumes were noted. The solution was then poured into a large volume of water. There was no evidence of a solid separating.

OXIDATION WITH NITRIC ACID - TRIAL 2

A saturated solution of the pseudonitrole in 20cc. of glacial acetic acid was prepared as before. This solution was added dropwise to about 20cc. of concentrated nitric acid warmed on a water bath. Brown fumes were again noted. Heating was continued until no more fumes could be seen. The solution was then poured into a large volume of water. There was no evidence of a solid separating.

OXIDATION WITH NITRIC ACID - TRIAL 3

A saturated solution of the pseudonitrole in 20cc. of glacial acetic acid was prepared. To this about 20cc. of concentrated nitric acid was added. No immediate change was noted

in the resulting blue solution. The solution was heated on a water bath to a temperature of 40° C. It was allowed to stand at this temperature for a period of five minutes at the end of which time the solution had turned green and brown fumes were given off. It was allowed to stand five more minutes at this temperature at the end of which time there appeared to be no change. The water bath was then heated to 50° C. and allowed to stand for ten minutes. At the end of this time the green appeared to have faded slightly. The water bath was then heated to 60° C. After standing five minutes at this temperature, the solution had turned brown. It was allowed to cool slowly to room temperature. On doing so the mixture became colorless. It was poured into a large volume of water. There was no evidence of a solid separating.

OXIDATION WITH POTASSIUM FERRICYANIDE

Propyl pseudonitrole (0.01 mole) was dissolved in approximately 20cc. of dioxan. This solution was mixed with one containing 33 grams of potassium ferricyanide (0.01 mole) and 2cc. of 29% potassium hydroxide (0.01 mole) in 200cc of water. This mixture was then refluxed for one hour. It was then divided into two parts, the first of which was steam distilled. No precipitate was noted in the distillate. The other portion was made slightly acidic with 3 N sulfuric acid and steam distilled. No precipitate was noted in the distillate.

OXIDATION WITH ACETYL PEROXIDE

The action of acetyl peroxide was tested on propyl pseudonitrole dissolved in carbon tetrachloride, glacial acetic acid, and ethyl acetate. To 0.001 mole of the pseudonitrole (0.12 gram) dissolved in 20cc. of the selected solvents, 2cc. of a 4% solution of acetyl peroxide in dimethyl phthalate was added. There was no change noted in any of the solutions at the end of one-half hour. At the end of 12 hours a slight precipitate was noted in the carbon tetrachloride solution. The precipitate was so slight that it could not be collected. The experiment was repeated using larger amounts but could not be duplicated. None of the other solutions showed any change.

OXIDATION WITH BENZOYL PEROXIDE

The action of benzoyl peroxide was tested on propyl pseudonitrole dissolved in carbon tetrachloride, glacial acetic acid, and ethyl acetate. To 0.001 mole of the pseudonitrole (0.12 gram) dissolved in 20cc. of the selected solvents, 0.24 gram of benzoyl peroxide was added. In each case a blank solution for color reference was prepared containing the same concentration of the pseudonitrole as before but without any peroxide being present. In no case was there any immediate decoloration. No change was noted at the end of one-half hour. The solutions were allowed to stand over night at the end of which time there was no change.

OXIDATION WITH UREA PEROXIDE

The action of urea peroxide was tested on propyl pseudonitrole dissolved in carbon tetrachloride, glacial acetic acid, and ethyl acetate. To 0.001 mole of the pseudonitrole (0.12 gram) dissolved in 20cc. of the selected solvents, 0.15 gram of urea peroxide was added. Blanks were run as before. There was no decoloration noted at the end of one-half hour. The solutions were allowed to stand for a period of thirty-six hours at the end of which time all solutions including blanks and peroxides had become colorless. All solutions containing the peroxide were saved for steam distillation.

INVESTIGATION OF COLORLESS PROPYL PSEUDONITROLE SOLUTIONS

It was noted previously that a solution of propyl pseudonitrole on standing becomes colorless even without there being any oxidizing agent present. An attempt was made to isolate the product of this reaction. A saturated solution of the pseudonitrole in about 20cc. of acetone was prepared. This was allowed to stand in a stoppered flask overnight at the end of which time the color had faded to a green. It was allowed to stand two more days at the end of which time it had become straw yellow in color. The solution was transferred to an evaporating dish and allowed to evaporate spontaneously. A tar residue remained. This was repeated using dioxan as a solvent with the same result.

OXIDATION WITH HYDROGEN PEROXIDE

TRIAL 1

The action of 30% hydrogen peroxide was tested on propyl pseudonitrole dissolved in carbon tetrachloride, glacial acetic acid, and ethyl acetate. To 0.001 mole of the pseudonitrole (0.12 gram) dissolved in 20cc, of the selected solvents, 2cc. of hydrogen peroxide was added. Blanks were run as before. There was no change noted in any of the solutions at the end of one-half hour. The solutions were allowed to stand for a period of thirty-six hours, at the end of which time all solutions including blanks and peroxides had become colorless.

The above peroxide solutions were mixed with those saved from the trial with urea peroxide. The peroxides in the resulting solution were destroyed by the addition of acidic aqueous ferrous sulphate. The mixture was then steam distilled. An organic layer and an aqueous layer resulted in the distillate. No solid appeared in the aqueous layer. The organic layer was separated and evaporated to dryness. No residue appeared.

OXIDATION WITH HYDROGEN PEROXIDE

TRIAL 2

A saturated solution of propyl pseudonitrole in 5cc. of glacial acetic acid was prepared. To this solution, 2cc. of 30% hydrogen peroxide was added. No immediate decoloration was noted. The solution was heated on a steam bath for five minutes at the end of which time the solution had become colorless. The reaction mixture was poured into a large volume of water. No solid separated.

The above experiment was repeated using larger quantities. Six tenths of a gram of the pseudonitrole was dissolved in 20cc of glacial acetic acid. Five tenths of a cc. of 30% hydrogen peroxide was added. The mixture was heated on a steam bath. At the end of seven minutes of slow heating the solution changed from a deep blue to a distinct green with the evolution of a brown gas. At this point heating was discontinued and the reaction mixture was allowed to stand in the water bath. At the end of five minutes the solution had become a faint yellow-green color. The mixture was poured into water. No solid separated. The residual peroxide was destroyed by acidic potassium permanganate. The resulting solution was steam distilled. No solid separated in the distillate. The distillate was extracted with ether. The ether extract was allowed to evaporate spontaneously. No residue remained. A portion

of the aqueous layer was allowed to evaporate. No residue remained.

OXIDATION WITH HYDROGEN PEROXIDE

TRIAL 3

Approximately 0.07 mole of 2-nitro propane (6 grams) was dissolved in 15cc. of 29% aqueous potassium hydroxide (0.1), by shaking in a heavy glass bottle. The temperature was kept at a minimum by adding cracked ice. When the solution had become complete the mixture was transferred to a three necked flask which contained an aqueous solution containing 0.072 mole of sodium nitrite (5 grams). The flask was equipped with an efficient stirrer, a thermometer, and a dropping funnel. Three normal sulfuric acid was added dropwise. The temperature of the reaction mixture was kept between -5° and + 5° C. by keeping the flask immersed in an ice bath and by adding cracked ice to the mixture as necessary. Acid was added until the solution had changed from a straw yellow to a blue color. A portion of the liquid was extracted with ether. The extract was allowed to evaporate. A solid residue remained which had a melting point of 65°-69° C. This and the fact that the solution was blue is a very good indication that some propyl pseudonitrole had been formed.

At this point a mixture of 0.09 mole of hydrogen peroxide (10cc. of 30% aqueous hydrogen peroxide) and 10cc. of 3 N sulfuric acid was added dropwise, the temperature being maintained between -5° and + 5° C. No immediate decoloration of the

solution was noted. Stirring was continued for fifteen minutes at the end of which time the color had faded to a light yellow-green and a precipitate had formed. The residual peroxide was destroyed by adding acidic potassium permanganate until the solution remained a faint pink. The mixture was steam distilled. A white solid separated in the distillate. This solid was collected and dried. It had a melting point of 210° C. There was not enough solid for any other tests.

OXIDATION WITH HYDROGEN PEROXIDE

TRIAL 4

The same procedure was followed as in trial 3 except for the fact that the mixture was filtered before the peroxide was destroyed with permanganate. The solid that was collected was recrystallized from a mixture of alcohol and water. It had a melting point of 211° C. corrected. The melting point was very unsatisfactory due to the fact that the solid in the capillary tube started to disappear at about 160° C. and very little was left at 211° C. when the first liquid was noted.

The solubility of the above substance differs greatly from that of the propyl pseudonitrole. It is quite soluble in carbon tetrachloride, alcohol, and ether. No shaking is required to make it go into solution. The solutions in all cases are colorless.

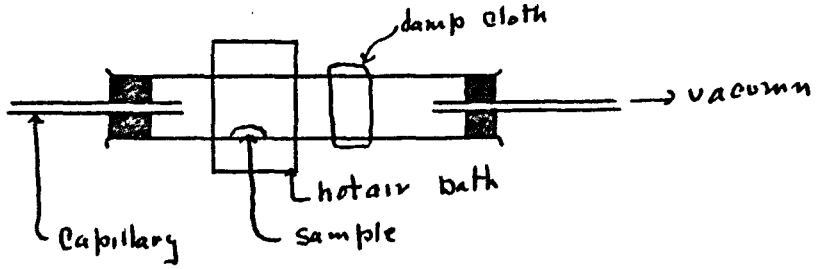
PURIFICATION OF COMPOUND RESULTING FROM HYDROGEN PEROXIDE OXIDATION

TRIAL 4

It was found that on ignition the compound that resulted from the hydrogen peroxide oxidation, trial 4, a residue remained. This residue was dark brown in color and was inappreciably soluble in water. The water-residue mixture did not affect litmus paper. This residue remained even after two recrystallizations from an alcohol-water solution.

It was noted before that during melting points taken on the substance it seemed to disappear. From this it was thought that the compound might sublime and furthermore that this might be a means of purification. The substance was tested and found to sublime readily. The sublimed material on ignition left no residue.

A schematic diagram of the sublimation apparatus is shown below.



A temperature between 70° and 90° C. at a pressure of 15 mm is sufficient.

ANALYSIS OF COMPOUND RESULTING FROM HYDROGEN PEROXIDE OXIDATION

TRIAL 4

An elementary analysis of the compound that resulted from trial 4 with hydrogen peroxide, proved the presence of nitrogen but no sulfur.

Carbon and Hydrogen Determination

Run	wt. of sample	wt. of CO_2	wt. of H_2O	% C	% H_2
1.	.01348	.01884	.00715	38.11	5.94
2.	.01571	.02381	.00962	40.39	6.85
3.	.01272	.01792	.00713	38.51	6.27
4.	.01313	.01908	.00779	39.63	6.64
5.	.00957	.01409	.00506	40.15	5.92
6.	.01043	.01595	.00646	41.7	6.93
7.	.01011	.01506	.00619	40.69	6.84

Runs 2,4,5, and 7, being in best agreement, were averaged resulting in 40.21% carbon and 6.56% hydrogen.

MOLECULAR WEIGHT DETERMINATION OF COMPOUND
RESULTING FROM HYDROGEN PEROXIDE OXIDATION
TRIAL 4

Solvent used - ethylene bromide

Weight of solvent - 38.3539

Molal freezing point depression per thousand grams of solvent[2] - 12.5

Run #1

weight of solvent 38.3539 grams

weight of solute .0185 grams

change in freezing point .035 C

molecular weight 172.4

Run #2

weight of solvent 38.3539 grams

weight of solute .0434 grams

change in freezing point .105

molecular weight 135

The value obtained in the first run is considered to be more accurate than that found in the second run due to the fact that the first solution is more dilute and therefor approaches ideal behaviour more than the second.

IDENTIFICATION OF COMPOUND RESULTING FROM HYDROGEN PEROXIDE OXIDATION

TRIAL 4

The previous analysis on the compound resulting from hydrogen peroxide oxidation - trial 4, led to an insight of what that compound might be. If it is assumed that the compound is bimolecular; that no carbon is lost by oxidation; and that the nitro group is not affected by the peroxide, the resulting compound would have six carbon atoms and from the analysis the molecular weight would be 176. This figure is in good agreement with the first run in the determination of the molecular weight. If the assumptions made are correct, then the resulting compound should be 2,3 dinitro-2,3-dimethyl butane. This compound was prepared and a mixed melting point taken.

The prepared 2,3-dinitro-2,3-dimethyl butane melted at 209°C. The mixture melted at 209.5°C. This fact in conjunction with the agreement of the two compounds with other physical properties prove, beyond reasonable doubt, that the two compounds are the same.

PREPARATION OF 2,3-DINITRO-2,3-DIMETHYL BUTANE[10]

A. Preparation of 2-Bromo-2-Nitro Propane

Twenty-two hundredths of a mole of 2-nitro propane (18cc.) was dissolved in .38 mole (45cc of 29% aqueous KOH) of aqueous potassium hydroxide. The solution was cooled and 0.2 mole of bromine was added dropwise with stirring. The 2-bromo-2-nitro propane separated as a liquid. It was washed with potassium hydroxide and water, and then dried over calcium chloride.

B. Preparation of 2,3-Dinitro-2,3-Dimethyl Butane

Fifteen hundredths of a mole of 2-nitro propane (13.5cc) was added to a solution of .15 mole (6 grams) of sodium hydroxide in 60cc of 50% alcohol. This solution was added dropwise to a refluxing mixture of 2-bromo-2-nitro propane (.15 mole) and alcohol, over a period of 3 hours. Heating was continued for another half hour and the mixture was allowed to cool. It was then diluted with water at which time a solid separated. It was filtered and recrystallized from alcohol and water. It had a melting point of 209° C.

DISCUSSION OF REACTION RESULTING IN THE PREPARATION OF 2,3-DINITRO-2,3-DIMETHYL BUTANE

It was felt that the reaction between 2-nitropropane, sodium nitrite, hydrogen peroxide, and sulfuric acid to form 2,3-dinitro-2,3-dimethyl butane needed further investigation. It was, therefor, attempted to discover the species that took part in the reaction. The function of the sodium nitrite in the reaction was first investigated. It was felt that a knowledge of this would tell whether propyl pseudonitrole was an intermediate. This question was further complicated by the reaction discovered by Noland and Nygaard in which propyl pseudonitrole is formed from the potassium salt of 2-nitropropane simply upon acidification, without there being any sodium nitrite present.

Experiments 1, 4, 5, and 6 were carried out to ascertain the function of the sodium nitrite. If the pseudonitrole is an intermediate in the reaction either an increase in yield or an increase in rate, or both, should be noted with an increase of nitrite. If a yield is obtained without the nitrite being present it does not necessarily mean that the pseudonitrole is not an intermediate due to the Noland-Nygaard reaction noted above.

Experiment 2 was conducted to find the effect of the temperature on the reaction. A decrease in yield would be

expected with an increase in temperature due to the loss of nitrous acid at the elevated temperature.

Experiments 3, 8, 9, and 11 were performed to find the effect of the acid concentration in the reaction. Also experiments were included to show whether the acid and peroxide should be added simultaneously. If the pseudonitrole is an intermediate there should be little if any of the dinitro compound formed at a pH greater than 7.

Experiment 7 was conducted to find out the effect of the peroxide concentration. Obviously one would expect an increase of the product with increasing concentration.

The original experiment of the oxidation with hydrogen peroxide, trial 4, was carried out in all cases with certain modifications. Experiments 1 to 6 employed the use of litmus paper as an indication of the end point. Later it was found that by using phenolphthalein a more exact and rapid end point could be reached. Experiments 7 through 11 employed that indicator. The amounts of 2-nitropropane and potassium hydroxide were kept constant but the other reagents were varied.

EXPERIMENT 1

Six cc. of 2-nitropropane was dissolved in 15cc. of 29% potassium hydroxide as before. Six normal sulfuric acid was added dropwise with stirring until the solution was faintly acid to litmus. At this point a mixture of 10cc. of 30% hydrogen peroxide and 10cc. of 6 N sulfuric acid was added dropwise with stirring. The temperature throughout the entire experiment was maintained between -5° and $+5^{\circ}$ C. No color change or precipitate was noted at the end of the addition. The mixture was taken out of the ice bath and allowed to warm slowly. At the end of five minutes a slight precipitate started to appear. The mixture was allowed to stand at room temperature until no more solid separated out. It was then filtered and the precipitate dried. The substance had a melting point of 208° C. The amount of precipitate was 0.6 gram.

EXPERIMENT 2

Experiment 1 was repeated excepting for the fact that after the 2-nitropropane was dissolved in the potassium hydroxide no more ice was added to the solution and the temperature was allowed to take its course. At no time during the addition of the sulfuric acid-hydrogen peroxide solution did the temperature of the reaction mixture exceed 20° C. The solution became cloudy during the addition of the last 5cc. of the acid-peroxide

solution. Twenty more cc. of the acid-peroxide solution was added. These were added dropwise but more rapidly than before. The temperature rose to 26° C. and the solution became a blue-green. The color faded in about five minutes and no increase in the cloudiness was noted. On standing overnight the precipitate had disappeared and the solution was colorless.

EXPERIMENT 3

2-Nitropropane (6cc.) was dissolved in 15cc of 29% potassium hydroxide as before. A mixture of 30cc. of 6 N sulfuric acid and 20cc. of 30% hydrogen peroxide was added dropwise to the basic solution with stirring. The temperature was maintained between -5° and +5° C. The solution turned a faint blue after about 30cc. of the acid-peroxide solution had been added. No precipitate was noted. At the end of the addition no change was noted. Stirring was continued for fifteen minutes at 0° C. at the end of which time the color had almost faded and no precipitate had appeared. The solution was allowed to stand overnight at room temperature. No change was noted.

EXPERIMENT 4

Six cc. of 2-nitropropane was dissolved in 15cc. of 29% potassium hydroxide as before. One tenth the theoretical amount (0.5 grams) of sodium nitrite for the formation of propyl pseudonitrole was added in the form of an aqueous solution. Sulfuric acid was added to the phenolphthalein end point.

A mixture of 10cc. of 6 N sulfuric acid and 10cc. of 30% hydrogen peroxide was added. The temperature was maintained at 0° C. and stirring was continued throughout the reaction. Upon the addition of the first few drops of acid-peroxide solution a solid started separating out. At the end of the addition the solution was a faint blue color. The yield was one gram of crude product. If the yield were calculated on the basis of the sodium nitrite, with the intermediate formation of propyl pseudonitrole, it would correspond to a percentage yield of approximately 175%.

EXPERIMENT 5

Experiment 4 was repeated except for the fact that a theoretical amount of sodium nitrite (4.5 grams) was added. The precipitate was formed at the very beginning of the addition of the acid-peroxide solution. The mixture was a distinct blue at the end of the reaction. The mixture was filtered and dried. It was then purified by sublimation. The crude yield was 1.3 grams and the purified yield was .95 grams. It had a melting point of 208° C.

Experiment 6

Experiment 4 was repeated using twice the theoretical amount of sodium nitrite (10 grams). The solid separated upon the addition of the acid-peroxide solution. At the end of the addition the solution was blue to deep green in color. The

impure yield was 1.27 grams and the pure yield was .76 grams. The melting point was 208°C.

EXPERIMENT 7

2-Nitropropane (6cc.) was dissolved in 15cc. of 29% potassium hydroxide as before. Five grams of aqueous sodium nitrite was added. The basic solution was taken to the phenolphthalein end point by adding 6 N sulfuric acid. A mixture of 10cc. of 6 N sulfuric acid and 20cc. of 30% hydrogen peroxide was then added dropwise. The temperature was maintained at 0°C. and stirring was continued throughout the entire reaction. A precipitate was noted when the acid-peroxide solution was added. The solution was filtered and the precipitate dried. The impure yield was 1.35 grams and the pure yield was 1.29 grams. The melting point was 210°C.

EXPERIMENT 8

2-Nitropropane (6cc.) was dissolved in 15cc. of 29% potassium hydroxide as before. To this an aqueous solution of 5 grams of sodium nitrite was added. Four grams of sodium peroxide was added to this mixture and the entire solution was allowed to stand overnight at room temperature. A very slight amount of precipitate was formed which when dry had a melting point of 210°C. The filtrate was divided into two parts, one of which was cooled to 0°C. by adding ice and a drop of phenolphthalein. The solution was taken to the end point by

adding 6 N sulfuric acid. At this point the solution was a blue-grey color. It was allowed to stand overnight at room temperature at which time the solution had become pink. It was taken to the phenolphthalein end point once again and allowed to stand overnight. This cycle was repeated for two weeks, at which time no precipitate had appeared. The solution was made distinctly acid. At this time it turned blue in color. On standing five minutes the solution had turned colorless and a slight precipitate had formed. Upon the addition of more acid no change was noted. The precipitate was so small that it could not be collected. The other portion of the filtrate was cooled to 0°C. by adding ice. It was then made distinctly acid with 6 N sulfuric acid. A pungent odor was given off and the solution turned blue with a white solid separated. This was filtered and dried. It had a melting point of 75°C. The pseudonitrole melts at 75°C.

EXPERIMENT 9

Six cc. of 2-nitropropane was dissolved in 15cc. of 29% potassium hydroxide as before. A solution of 5 grams of aqueous sodium nitrite was added. The temperature was lowered to 0°C. by adding cracked ice and by keeping the reaction flask in an ice bath. Three normal sulfuric acid was added dropwise to the phenolphthalein end point. Ten cc. of 30% hydrogen peroxide was then added to the solution; the temperature being maintained 0°C. throughout. Upon the addition of

the peroxide solution the solution became yellow-green in color. No precipitate was noted. Stirring was continued for fifteen minutes at 0°C. No change was noted. The solution was allowed to come to room temperature and allowed to stand overnight. At the end of this time a precipitate had formed. It was filtered and dried. A melting point of 212°C. was obtained. The crude yield was .18 grams.

EXPERIMENT 10

2-Nitropropane (6cc.) was dissolved in 15cc. of 29% potassium hydroxide as before. An aqueous solution of five grams of sodium nitrite was then added. The solution was then taken to the phenolphthalein end point by adding 6 N sulfuric acid dropwise with stirring. Ten cc. of 30% hydrogen peroxide was then added. At the end of this addition 10cc. of 6 N sulfuric acid was added. The temperature was maintained at 0°C. throughout. No precipitate was noted until the addition of the first part of the second acid addition. At the end of the reaction the solution was blue in color. The mixture was allowed to stand overnight at the end of which time the solution was filtered and the precipitate dried. A melting point showed that the substance contained a large amount of propyl pseudonitrole. An attempt was made to purify it by sublimation but this proved to be impractical, due to the large amount of pseudonitrole present.

EXPERIMENT 11

Experiment 10 was repeated excepting for the fact that the mixture was filtered at the end of the reaction. A melting point gave no indication that the pseudonitrole was present to any extent. A sharp melting point at 212°C. was obtained. The crude yield amounted to 1 gram.

DETERMINATION OF THE AMOUNT OF PROPYL PSEUDONITROLE IMPURITY IN THE PRODUCTION OF 2,3-DINITRO-2,3-DIMETHYL BUTANE

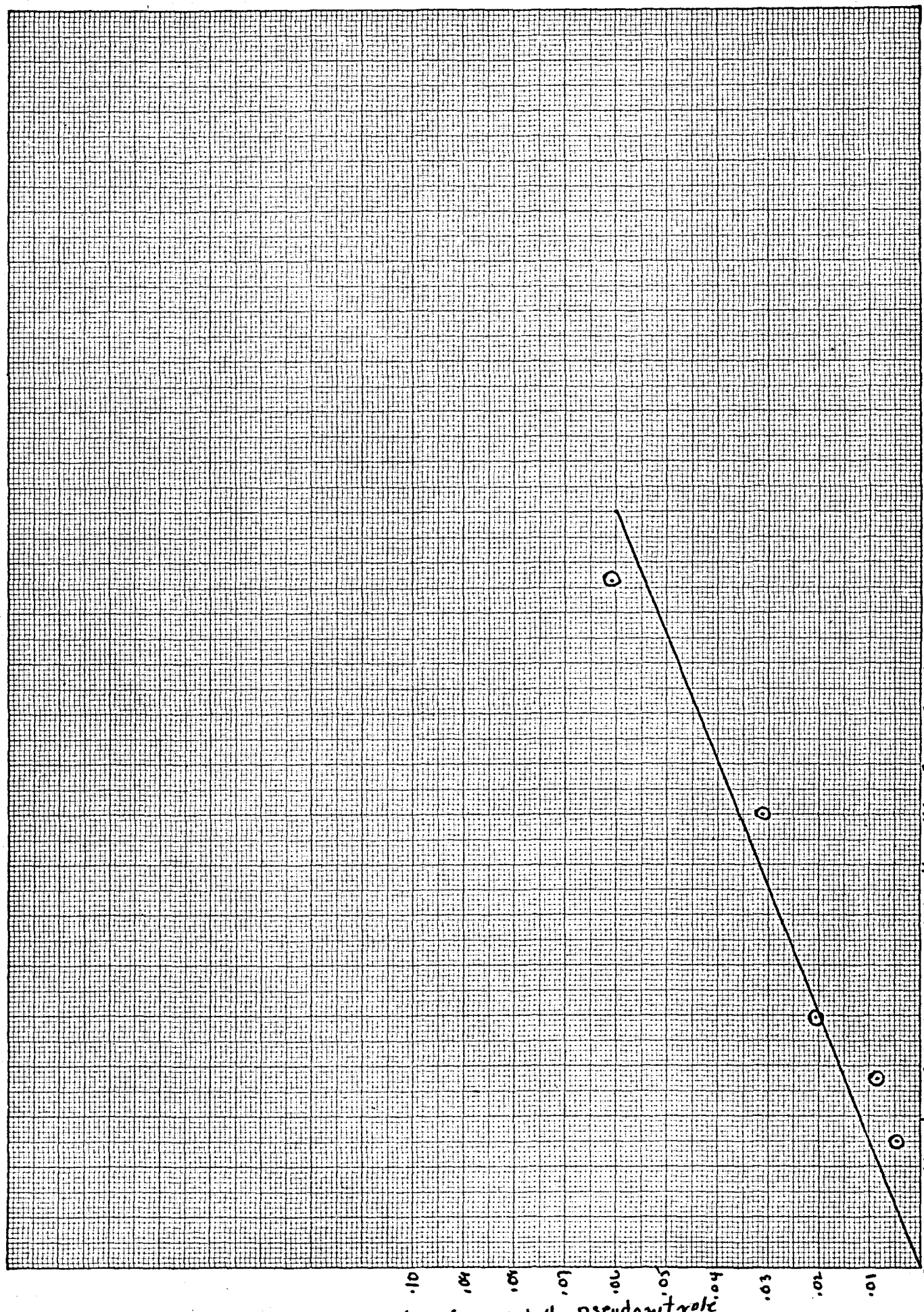
As an aid to discover the mechanism in the formation of 2,3-dinitro-2,3-dimethyl butane an analysis of the amount of propyl pseudonitrole present in the products was carried out. It was found possible to take advantage of the blue color of the pseudonitrole solution and carry out the analysis by employing a photoelectric colorimeter. Experiments 4, 5, and 6 were chosen for analysis as being typical in the amount of pseudonitrole formed.

To calibrate the colorimeter various weights of pseudonitrole were dissolved in 5cc. of dioxan and the corresponding scale reading taken. A plot was then made of amount of pseudonitrole vs. scale reading. Knowing the reading of an unknown it was then possible to read the amount of pseudonitrole directly from the graph.

In the analysis of the products, the yields were dissolved in 100cc. of dioxan. A 5cc. portion was then taken for the analysis. The weight taken from the graph must therefor be multiplied by twenty to find the weight per sample.

CALIBRATION OF PHOTOELECTRIC COLORIMETER

Weight of Pseudonitrole	Reading
0.0	0
0.0049	50
0.0083	75
0.0208	99
0.0311	180
0.0609	273



ANALYSIS OF PRODUCTS

Exp.	Weight of Sample	Reading	Weight of Pseudonitrole	% by weight
4	0.7643	15	0.06	7.9
5	0.6927	15	0.06	8.7
6	0.6073	5	0.03	4.9

For a more satisfactory analysis more points should be plotted at low concentrations.

TABULATION OF EXPERIMENTAL RESULTS

In all the experiments 0.07 mole of 2-nitropropane was dissolved in 0.1 mole of aqueous potassium hydroxide. The acid employed was 6 N sulfuric. Thirty percent hydrogen peroxide was used as the oxidizing agent unless otherwise stated.

Exp.	Moles $NaNO_2$	Experimental	% Yield
1.	0	neutralized solution with acid-added 20cc. of 50-50 mixt. of acid-peroxide temp. 0° C.	9.8
2.	0	neutralized solution with acid-added 20cc. of 50-50 mixt. acid-peroxide-added 20cc. acid-temp. 26° C.	0.0
3.	0	mixture of 30cc. of acid and 20cc. peroxide added to basic solution-temp. 0° C.	0.0
4.	0.0085	added to basic solution-temp. 0° C. neutralized solution with acid-added aqueous $NaNO_2$-added mixture of 10cc. acid and 10cc. peroxide-temp. 0° C.	16.2
5.	0.076	same as experiment 4	21.2
6.	0.17	same as experiment 4	20.6
7.	0.076	same as experiment 4 using a mixture of 10cc. of acid and 20cc. of peroxide	22.0
8.	0.076	added 0.07 mole of Na_2O_2 to basic solution	trace
9.	0.076	neutralized solution with acid-added 10cc. peroxide-temp. on addition 0° C.-solution allowed to stand overnight at room temp.	2.9
10.	0.076	neutralized with acid-added 10cc. peroxide-added 10cc. acid-allowed solution to stand overnight-large amount of pseudonitrole in product	-
11.	0.076	same as experiment 10-filtered immediately after addition of acid	16.2

AN INTERPRETATION OF THE EXPERIMENTAL RESULTS

An interpretation of the experimental results at this point would be quite inconclusive, due to the incompleteness of the data. Yet a few broad generalizations seem to follow directly from the preceding experiments. In the first place, the sodium nitrite seems to play an important part in the reaction, either as a catalyst or in the formation of an intermediate. In all cases when a peroxide-acid solution was added to a mixture that contained sodium nitrite a precipitate formed almost immediately.

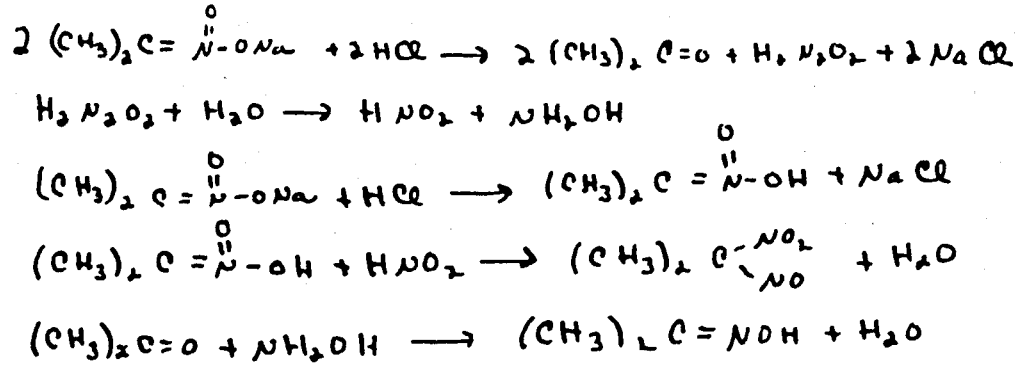
The fact that some compound was formed without there being any nitrite ion present does not oppose the above statement. It will be recalled that Noland and Nygaard[3] obtained pseudonitrole without nitrite ion being added. This, however, does not prove that the pseudonitrole is an intermediate because Noland and Nygaard envisioned nitrous acid being formed as an intermediate in their reaction.

It might be well at this point to review their work including the mechanism that they presented. They have found that both nitrolic acids and pseudonitroles can be prepared by dissolving a nitroparaffin in aqueous alkali and then acidifying the resulting solution at a temperature below 15°C. with a mineral acid other than nitrous acid. The products and the yields for the reaction are given in the chart below. The

reaction is for the preparation of propyl pseudonitrole.

products recovered	oxygen atmosphere		nitrogen atmosphere	
	parts by weight	percent theoretical	parts by weight	percent theoretical
2 nitro propane	37.5	42.1	9.1	10.2
propyl pseudonitrole	17.6	29.8	35.4	60.0
acetone	10.3	35.6	17.6	60.6
acetone oxime	5.5	7.5	8.6	11.8

The authors have given two mechanisms in the literature the first of which they have discarded due to the fact that it does not explain the formation of the acetone oxime. The second and more acceptable is given below.[9] The first two steps are the only questionable ones advanced. Whether such disproportionations are possible or not is questionable. If they do occur the final three steps are straightforeward.



In the preparation of the dinitro compound with hydrogen peroxide all solutions appeared to be buffered. This fact indicates the peroxide reaction. In the literature three reactions for the decomposition of hydrogen peroxide are given as follows:[4]

1) $H_2O_2 = O_2 + 2H^+ + 2\epsilon^-$ $\quad -.68$
2) $3OH^- = HO_2^- + H_2O + 2\epsilon^-$ $\quad -.87$
3) $2H_2O = H_2O_2 + 2H^+ + 2\epsilon^-$ $\quad -1.78$

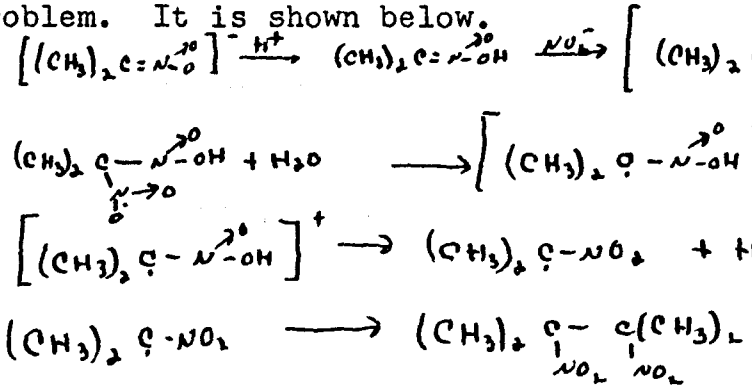
It would seem that the peroxide undergoes the second or third reaction if the buffering effect is remembered.

In the solution there are at least two species capable of being oxidized. The first and most obvious is the nitrite. From the experimental evidence it seems certain that this does not take place if the acid and peroxide are added simultaneously. If the nitrite were being oxidized by the peroxide it would then seem to follow that the amount of nitrite and peroxide would have nothing to do with the formation of the dinitro compound. As shown by the experimental evidence, the presence of nitrite not only increases the rate of the reaction but also the yields to a certain extent. Also if the nitrite were being oxidized nitrate alone should bring about the reaction. This question has not been investigated completely but a test run has shown that if the reaction does take place with nitrate in the presence of peroxide it is at a slow rate with low yields.

It would seem from the previous argument that there is another species in the reaction that is more easily oxidized than the nitrite. It also seems clear that this intermediate is not propyl pseudonitrole as such due to the fact that all the

attempts to oxidize that compound did not result in the formation of any 2,3-dinitro-2,3-dimethyl butane.

A mechanism has been suggested by Dr. Lichtin[7] not as an answer to the problem but as a starting point for the mechanistic problem. It is shown below.



If the above mechanism was correct in all respects one would expect the dinitro compound to be formed upon the addition of peroxide to a neutral solution of the potassium salt of 2-nitropropane and sodium nitrite. It was found that this was true but that the yield was very small.

It is felt that any further discussion of the mechanism should be preceded by a more exhaustive study of the reaction.

REACTION OF 2-NITROPROPANE WITH ETHYLCHLOROCARBONATE

Seven hundredths of a mole of 2-nitropropane was dissolved in 0.1 mole of aqueous potassium hydroxide (15cc. of 29% KOH). The temperature was kept at a minimum by adding cracked ice. This solution was then transferred to a three necked flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel. Ethylchlorocarbonate was added dropwise with stirring. No precaution was taken with the temperature which increased from 15° C. to 40° C. during the addition. The solution turned blue and a blue liquid was noted separating. Stirring was continued until the temperature fell to 35° C. At this point the liquid had changed into a blue solid. The solution was acid to litmus at this point. The solid was separated by filtration. On drying the solid became white. A melting point was found to be 209° C. The compound was purified by sublimation and a mixed melting point with the compound that was produced from the hydrogen peroxide oxidation-trial 4 was taken. There was no depression in the melting point.

The same reaction was repeated with .1 mole excess of potassium hydroxide. The same separation of a liquid which changed into a solid was noted. Stirring was continued for some length of time during which the solid became white even when wet. The pH of the solution at the end point was seven. A portion of the reaction liquid was acidified resulting in

the evolution in a large amount of colorless, odorless gas.

ANALYSIS OF CARBON DIOXIDE LIBERATED IN THE REACTION BETWEEN 2-NITRO PROPANE AND ETHYLCHLOROCARBONATE

It was felt that a knowledge of the amount of carbon dioxide liberated in the reaction between ethylchlorocarbonate and the sodium salt of 2-nitropropane might lead to an understanding of the function of the ethylchlorocarbonate. An air-tight apparatus was set up so that all the carbon dioxide liberated in the experiment could be collected in carbonate free sodium hydroxide. It consisted of a three necked flask equipped with a dropping funnel, a mercury sealed stirrer, and an exhaust lead connected to an adsorption train. The train was made up of four six-inch test tubes the first of which contained aqueous acidic silver nitrate to collect any ethylchlorocarbonate that might be carried over or any hydrogen chloride that might be evolved during the reaction. The remaining three test tubes contained 15cc. of known concentration sodium hydroxide.

2-Nitropropane (0.105 mole) was placed in the flask and nitrogen gas was passed through it via the dropping funnel for one-half hour. During the entire time stirring was continued. The flask was then surrounded by an ice bath and 25cc. of 6.89 N sodium hydroxide was added. Stirring was continued until the solution was complete. Ethylchlorocarbonate (0.105 mole) was then added to the solution by forcing it down the dropping

funnel with nitrogen. The reaction proceeded as before. A white precipitate was noted forming in the test tube containing the silver nitrate. A gas was later noted being adsorbed by the sodium hydroxide. Nitrogen gas was passed through the flask the entire time. After the reaction had ceased and no more gas was being adsorbed nitrogen was passed through the apparatus for one half hour.

The sodium hydroxide in the three test tubes was mixed intimately and a 10cc. portion was diluted to 100cc. Ten cc. portions of this solution were then analyzed for carbonate by titrating with standard hydrochloric acid both the carbonate and the hydroxide to the bromphenol blue end point while in another sample the carbonate was precipitated as barium carbonate and the hydroxide titrated to the phenolphthalein end point. The difference in the two readings represents the amount of acid required for the carbonate." The results are tabulated below.

Normality of original base - 6.89

Volume of base used for adsorption - 45cc.

Normality of standard acid - 0.525

Volume of acid required for carbonate - 4.34cc.

Weight of CO_2 in 10cc of the diluted solution - 0.0504

Total weight of CO_2 evolved during reaction - 2.26

Percent of theoretical amount of CO_2 - 60%

Percent yield of 2,3-dinitro-2,3-dimethyl butane - 6.4%

REACTION OF 2-NITRO PROPANE WITH SULFURYL CHLORIDE

Seven hundredths of a mole of 2-nitropropane (6 grams) was dissolved in 15cc. of 29% potassium hydroxide (0.1 mole) by shaking in a heavy walled glass bottle. The temperature was kept at a minimum by adding cracked ice. This solution was then transferred to a three necked flask equipped with a dropping funnel, a thermometer, and a mechanical stirrer. Sulfurylchloride (0.07 mole) was added dropwise. During the addition a blue liquid separated to the top of the reaction mixture. After all the sulfuryl chloride had been added stirring was continued for fifteen minutes, at the end of which time no change could be noted in the reaction mixture. A portion of the blue liquid was taken and tested for acidity. It had a pH of 1. Sodium bicarbonate was added until the pH became 8. At this point the blue liquid had disappeared. The solution was made acidic by adding 5% hydrochloric acid. The blue solution did not return nor was there any evidence of a precipitate.

Another portion of the blue liquid was ignited. It burned and left no residue.

The final portion of the liquid was allowed to stand overnight in a stoppered bottle. There was no change noted. It was then placed on a watch glass and allowed to evaporate. A white solid remained which had a melting point of 205° C. It

was very impure as indicated by the melting point. The amount of the solid was just enough to take two or three melting points.

It seems quite certain that this compound is 2,3-dinitro-2,3-dimethyl butane. In the first place it seems likely that the sulfuryl chloride would chlorinate the potassium salt of 2-nitropropane forming 2-chloro-2-nitropropane. The chloro derivative could then combine with the potassium salt of 2-nitropropane forming the 2,3-dinitro-2,3-dimethyl butane. It was felt that the blue liquid containing this substance is a mixture of unreacted sulfuryl chloride and 2-chloro-2-nitro-propane. Working on this assumption an attempt was made to fractionally distill the liquid. This proved unsuccessful.

PREPARATION OF N-NITROSODIMETHYLAMINE [5]

To 1.1 moles of aqueous dimethylamine (150cc. of 30% aqueous dimethylamine) enough 3 normal sulfuric acid was added to make two drops of methyl red indicator, which had been added to the solution, distinctly pink. Sixty-five hundredths of a mole of aqueous sodium nitrite (45 grams of sodium nitrite in 50cc. of water) was added dropwise to the solution with efficient stirring. The solution was kept acidic to litmus by adding 3 normal sulfuric acid as necessary. No precautions were taken with the temperature.

When all the sodium nitrite solution had been added the solution was distilled almost to dryness. The distillate was acidified with 3 normal sulfuric acid and distilled once again. The N-nitrosodimethylamine in the distillate was salted out with potassium carbonate, and dried over anhydrous potassium carbonate. The boiling point was found to be 147°-148° C. The boiling point reported in the literature is 148° C.

OXIDATION OF N-NITROSODIMETHYLAMINE

The action of hydrogen peroxide, benzoyl peroxide, and acetyl peroxide was tested on N-nitrosodimethylamine. Due to the fact that the amine is a liquid in which all the peroxides are soluble there was no need to find a mutual solvent. In each case 0.05 mole (3.6cc) of the amine was used. Equivalent molar quantities of 30% hydrogen peroxide and acetyl peroxide (4% active oxygen in dimethyl phthlate) were employed. It was found impractical to use an equivalent molar quantity of benzoyl peroxide due to the high molecular weight of that compound. Two hundredths of a mole (4 grams) of that oxidizing agent was used. The peroxide-amine solutions were allowed to stand for four days at the end of which time there was no noticeable change in any of the solutions. At the end of the four day period the peroxides were destroyed with potassium permanganate and each mixture was then refluxed for a period of one-half hour. The purpose of this proceedure was to separate any N-nitrodimethylamine that was formed from the N-nitroso compound. The N-nitro compound being easily sublimeable should collect on the comdenser at a point higher than the condensing liquid. In no case was there evidence of a solid.

ABSTRACT

This research was undertaken to test the action of various oxidizing agents on two typical aliphatic nitroso compounds, propyl pseudonitrole and N-nitrosodimethylamine. The oxidizing agents tested include benzoyl peroxide, acetyl peroxide, 30% hydrogen peroxide, urea peroxide, potassium ferricyanide, and nitric acid.

To test the reaction with pseudonitrole it was necessary to dissolve that compound in various solvents including carbon tetrachloride, ethyl acetate, and glacial acetic acid. With the N-nitrosodimethylamine it was found possible to dissolve the peroxides in the amine itself. The N-nitroso compound was not tested with potassium ferricyanide or nitric acid.

In no case was it possible to separate a product resulting from the oxidizing of the nitroso group to the corresponding nitro compound. However two preparations of 2,3-dinitro-2,3-dimethyl butane from the potassium salt of 2-nitropropane were found. The first preparation consists of the solution of 2-nitropropane in slight excess of 29% aqueous potassium hydroxide. A molar quantity equal to that of the 2-nitropropane of aqueous sodium nitrite is then added. The resulting solution is then taken to the phenolphthalein end point by adding sulfuric acid. At this point a mixture of 10cc. of 6 N sulfuric acid and 10cc. of 30% hydrogen peroxide is added dropwise. The temperature throughout the entire reaction is maintained between -5° and $+5^{\circ}$ C.

The dinitro product separates and may be filtered. This reaction was investigated further to get some idea of the mechanism envolved. It was found that the amount of nitrite present effects the rate of the reaction and to some extent the yield.

The second preparation involves the addition of ethylchlorocarbonate to a solution of 2-nitropropane in potassium hydroxide. The dinitro compound separates as a blue liquid which changes to a blue solid which inturn changes to a white solid on filtration if the base and the nitropropane are present in equal molar quantities. If there is an excess of base present the blue solid becomes white while in the reaction mixture.

It was also found that 2,3-dinitro-2,3-dimethyl butane is formed by the action of sulfurylchloride on the potassium salt of 2-nitropropane. It was felt that this reaction is not novel but proceeds through the formation of 2-chloro-2-nitro propane which later reacts with the sodium salt of 2-nitropropane.

It is felt that further investigation is needed to arrive at a satisfactory mechanism for all three of the above reactions.

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