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# The reactions of l-chloro-l-nitro propane in anhydrous liquid ammonia

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THE REACTIONS OF 1-CHLORO-1-NITRO PROPANE  
IN  
ANHYDROUS LIQUID AMMONIA

A thesis presented to the Department of Chemistry of  
Union College, in partial fulfillment of the requirements  
for the degree of Bachelor of Science in Chemistry

by James S. Givens

Approved by F. C. Schmuck

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THE REACTIONS OF 1-CHLORO-1-NITRO PROPANE  
IN ANHYDROUS LIQUID AMMONIA

INTRODUCTION

In 1939 Seigle and Hass<sup>(1)</sup> were successful in preparing numerous dinitro paraffins such as 2,3-dimethyl-2,3-dinitro butane and 2,3-dimethyl-2,3-dinitro pentane by the reaction of salts of nitroparaffins with halonitroparaffins. They were unable to do so however, in the cases where primary nitro compounds were involved.

More recently, in an unpublished work Sottysiak believed that he prepared the 2,3-dimethyl 2,3-dinitro butane by a Wurtz reaction in liquid ammonia, in which 2-nitro-2-chloro propane was reduced by sodium.

Because of the strong reducing properties of a solution of sodium in anhydrous liquid ammonia, it was hoped that the 3,4-dinitro hexane could be prepared in this manner.

Sodium, when added to the nitro alkanes evolves hydrogen to form the sodium salt of the pseudo acid, according to the reaction:



A similar reaction was expected when the chloro-nitro propane was added to the liquid ammonia, but this should not affect the Wurtz reaction.



## EXPERIMENTAL

## THE REACTION OF 1-CHLORO-1-NITRO PROPANE WITH ANHYDROUS LIQUID AMMONIA

It was necessary, before proceeding with the Wurtz reaction in liquid ammonia, to determine if the chloro-nitro propane would react with the ammonia alone. For this, the commercial product, donated by Commercial Solvents Corporation was re-distilled and collected between a range of 140° to 142° Centigrade. The density and index of refraction were determined as:

$D_{20}$	1.210
$n_D$	1.4313

Approximately forty-eight grams of the liquid were added drop by drop to three hundred cubic centimeters of liquid ammonia at its boiling point. Upon addition the solution began to boil, and the solid chloro-nitro-propane crystalized out. With stirring the solid dissolved to form a light port colored solution. There was no apparent evolution of gas.

The solution was allowed to evaporate over night, leaving a white solid. This was weighed and found to be about 54 grams.

The ratio of the weights of the chloro-nitro propane and of the solid formed was found to be:

$$\frac{\text{Wt. CH}_3\text{CH}_2\text{CHClNO}_2}{\text{Wt. Solid}} = 0.888$$

while the ratio of the chloro-nitro propane to the ammonium salt of the pseudo acid is

$$\frac{\text{CH}_3\text{CH}_2\text{CHClNO}_2}{\text{CH}_3\text{CH}_2\text{CClNO}_2\text{NH}_4} = 0.879$$

While this is no proof that the ammonium salt was formed, we can assume a 1 : 1 ratio, and hence that one mole of ammonia was involved per mole of the chloro-nitro propane.

The white solid decomposed slowly on standing with the evolution of ammonia. This apparently is no simple decomposition of the ammonium salt of the pseudo acid. It also decomposes on the addition of water, or one-tenth normal nitric acid. For this investigation air was first blown into the solid. Ammonia was evolved and heat was given off. The solid first turned bright yellow, and then an oil appeared. This mixture was then acidified with one-tenth normal nitric acid. More of the redish-orange oil separated out and was drawn off. The oil was partially soluble in the aqueous solution. The greater part of this was removed by repeated extractions with ether. The oil and ether extractions were then dried with anhydrous magnesium sulfate, and the ether distilled. The total remaining oil weighed 24.4 grams. This distilled over a range from 125° to 170° at which point decomposition began to take place. The lower fractions were a light yellow oil.

Gas was evolved during the slow evaporation of



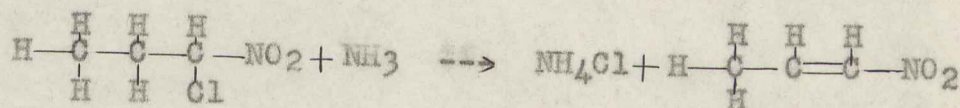
the aqueous solution. This was tested for ammonia, but with no positive results. The 13.0 grams of solid crystalizing from the aqueous solution were then tested. It was soluble in hot alcohol, and insoluble in dry ether even when hot. Ammonia was evolved upon the addition of sodium hydroxide. An aqueous solution reacted with silver nitrate solution to precipitate silver chloride.

The solid was analyzed for chloride ion by titration with one-tenth normal silver nitrate solution. Assuming the salt present was ammonium chloride, 63.5% of the thirteen grams was in that form.

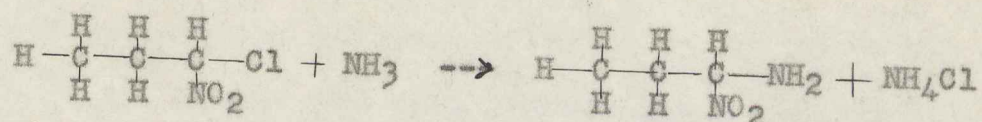
To prove that this was actually the case, a small sample of the solid was dissolved in hot alcohol, and recrystallized by the addition of ether. After drying, this was analyzed for chloride ion, and determined to be 99.69% ammonium chloride. It is evident that 0.154 moles or 39 to 40% of the original chloro-nitro propane had reacted with the liquid ammonia to form ammonium chloride.

The following reactions making possible the formation of ammonium chloride were postulated:

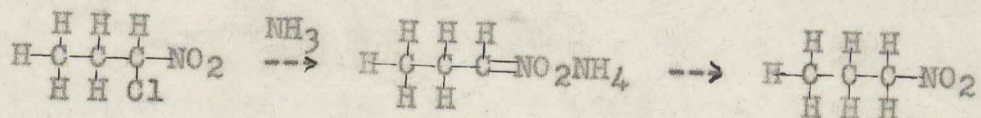
1. The formation of the unsaturated compound nitro-propylene



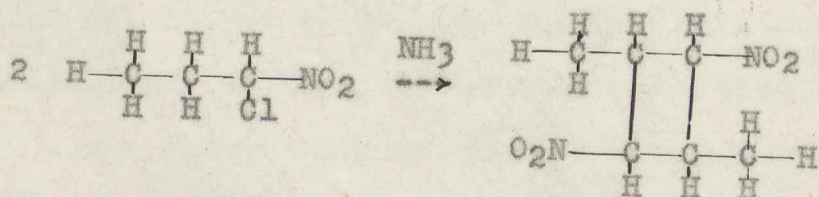
2. The formation of 1-amino-1-nitro propane



3. The formation of nitropropane by a reaction similiar to that of dibrom-dinitro methane, which was studied by Kraus, (2) and later by Cole, (3)



4. The formation of a ring compound by two molecules.



Following the same procedure as in the first run, 121.0 grams of the chloro-nitro propane were added to liquid ammonia, the resulting solid decomposed, and the oil extracted. The water extraction was again analyzed for ammonium chloride, and the previous conclusion checked, that about 40% of the original substance had lost chlorine.

Because of the decomposition encountered in the distillation of the oil, this was now done in partial vacuum. A trial run showed two temperature ranges, the first from 35° to 45° Centigrade, and the second



from  $55^{\circ}$  to  $65^{\circ}$ , the pressure being 16 mm. of mercury.

Glass wool was then packed in the neck of the distilling column to insure greater separation. As a result of several distillations, two sizable fractions with fairly constant boiling points were obtained.

The first of these boiled at  $35^{\circ}$  to  $39^{\circ}$  under 16 mm. pressure. It was soluble in alcohol, ether, and in six normal sodium hydroxide, insoluble in water and dilute acids. The product of a sodium fusion showed positive tests for chlorine and nitrogen. An amine was formed when the oil was reduced by tin and hydrochloric acid. Evidently this fraction is the original compound. It was redistilled at normal pressure the boiling range being  $139^{\circ}$  to  $142^{\circ}$ . The density and index of refraction were determined as:

$D_{20}$	1.205
$n_D$	1.4359

There were 24.5 cubic centimeters of colorless liquid in this fraction.

The second fraction distilled over a range of  $55^{\circ}$  to  $59^{\circ}$  under a pressure of 16 mm. of mercury. It was light yellow in color. An analysis of the sodium fusion product again showed the presence of chlorine and nitrogen, and the latter was found to be present in the nitro group. In addition the following



tests were applied. No reaction was apparent on the addition of bromine in carbon tetrachloride. A small amount of potassium permanganate solution was decolorized. With alcoholic silver nitrate, it reacted slowly to precipitate silver chloride. Hydrogen was slowly evolved by metallic sodium. Hinsberg's test for amines was negative. Benzenesulfonyl chloride was added to a 10% sodium hydroxide solution of the oil. The solution was of a yellowish color, there being no residue. A blue oil separated out on acidifying this solution. The index of refraction was determined as:

$$n_D \quad 1.4238$$

A small sample, 5 cubic centimeters, of this fraction was redistilled at normal pressure. The boiling point for all except that last half cubic centimeter was from  $141^{\circ}$  to  $143^{\circ}$ . Above that temperature decomposition took place. The oil remaining in the distilling flask was again fused with sodium, and the presence of nitrogen and chlorine confirmed.

A dark red, very viscous oil remained in the flask from the vacuum fractional distillation. From this about four-tenths of a gram of a white, paraffin-like solid were crystalized and then dried between filter paper. The solid was soluble in alcohol, ether, and sodium hydroxide solution, and insoluble in water, 5% sodium bicarbonate, and acid solutions. Analysis for chlorine and nitrogen gave no positive test, but



this is not reliable since the amount available for testing was so small that this could not be confirmed. The boiling point of the solid was  $90^{\circ}$  to  $94^{\circ}$  under 16 mm. pressure.

The remaining four cubic centimeters of red oil were then tested. It was soluble in ether, alcohol, and sodium hydroxide solution, and insoluble in water and acid solutions. Analysis of the sodium fusion product showed the presence of chlorine and nitrogen. Metallic sodium reacted slowly to evolve hydrogen. There was no reaction with bromine in carbon tetrachloride, or aqueous potassium permanganate. Hinsberg's test for amines gave a negative result.

#### DISCUSSION

From the reactions and boiling points of the second fraction it appears that it consisted of a constant boiling mixture of at least two very similiar liquids. One of these was the original chloro-nitro propane, as indicated by the presence of chlorine and nitrogen in a nitro group. The failure to add bromine does not necessarily indicate the absence of unsaturated compounds, since the presence of negative groups on the carbon atoms of an ethylenic bond causes the addition to be slow and in extreme cases may inhibit the reaction. The proposed nitro propylene has the nitro group on the alpha carbon, and hence may do



this. The reduction of the permanganate solution was extremely weak and hence likewise does not indicate the presence of unsaturation. It must be remembered that an amine will also reduce the later, but this is apparently not the case since the Hinsberg test was negative.

Since it was evident that no separation of this mixture would be attained by further distillation, attempts were made to extract one or the other of the components by their differences in solubility. This was unsuccessful, since no suitable solvent was found. If one of the components is the proposed nitropropane, it may be possible to separate it by reduction to the amine. This was not attempted because of lack of time.

The large amount of residue which was not ammonium chloride in the solid resulting from the evaporation of the aqueous extraction, together with the fact that approximately half of the oil disappeared during the reaction with ammonia indicates that possibly one of the reaction products is a solid, which is soluble in water. Moreover, the evolution of gas during the evaporation cannot be accounted for.

Assuming ammonium nitrate was formed during the acidification of the aqueous solution, the amount used, about two hundred cubic centimeters of one-tenth normal, does not account for all of the residue.

All attempts to separate this mixture by dissolving it



in organic solvents and recrystallizing were unsuccessful because of the solubility of the ammonium chloride, or resulted in the recovery of minute amounts of the red oil residue already discussed. Attempts to remove the ammonium chloride by precipitating the chloride ion as silver chloride were also unsuccessful.

#### THE REACTION OF 1-CHLORO-1-NITRO PROPANE WITH SODIUM IN ANHYDROUS LIQUID AMMONIA

Since some of the chloro-nitro propane entered no reaction other than forming the ammonium salt of the pseudo acid, one trial of the Wurtz reaction was performed. Sodium was dissolved in the liquid ammonia at its boiling point, and the chloro-nitro propane added to the solution drop by drop. The mixture immediately boiled strongly. Two moles of sodium had been added to the ammonia for every mole of chloro-nitro propane that was to be reacted, since one mole would probably form the sodium salt of the pseudo acid, leaving the other mole of sodium to enter the Wurtz reaction. However, the blue color of the sodium solution disappeared, indicating that all of the sodium had been reacted when only about half of the organic liquid had been added. Analysis of the inorganic products showed the presence of sodium hydroxide, probably formed by oxidation by air of the sodium during the boiling of the solution. The only organic matter that could be extracted was a redish



oil, which reacted similarly to that obtained in the reaction of the chlor-nitro propane with the ammonia alone.

#### CONCLUSION

When 1-chloro-1-nitro propane is added to anhydrous liquid ammonia, part of it reacts with the ammonia to form the ammonium salt of the pseudo acid. About 40% reacts further to lose chlorine, as indicated by the formation of ammonium chloride. There was little evidence to show that this was done either by unsaturating the liquid or by forming an amine. Probably the reaction is very complex, resulting in several compounds and in the decomposition of the chloro-nitro propane into volatile liquids or gases.

The one attempt to perform a Wurtz reaction on 1-chloro-1-nitro propane in liquid ammonia was unsuccessful.

