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The preparation of chlorobromo dinitromethane and its reaction with liquid ammonia

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THE PREPARATION OF CHLOROBROMO DINITROMETHANE
AND ITS REACTION WITH LIQUID AMMONIA

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E. N. Case

Presented to the Department of Chemistry of Union
College in partial fulfillment of the requirements for the
degree of Bachelor of Science in Chemistry.

Presented by Edward H. Case

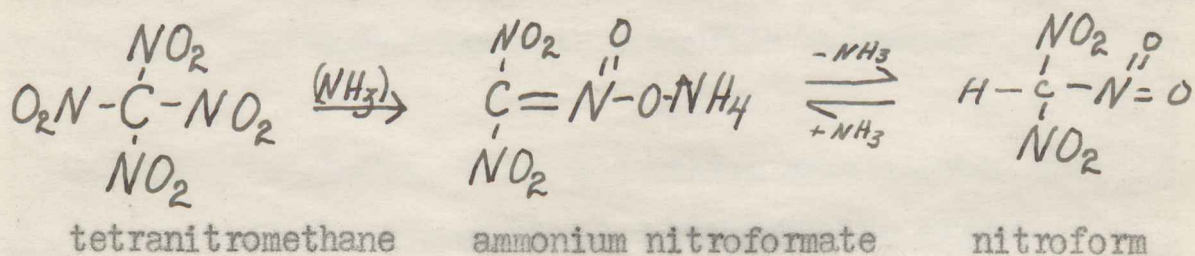
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THE PREPARATION OF CHLOROBROMODINITROMETHANE AND ITS REACTION WITH LIQUID AMMONIA

The nitro-alkyls have been recorded in the literature for many years. The preparation of the lowest completely nitrated hydrocarbon, tetranitromethane, from acetic acid, acetic anhydride, and fuming nitric acid, has been described by Berger. (1) On reaction with liquid ammonia it forms a salt of nitroform (2).



Nitroform can be converted into tetranitromethane by dissolving in a heated mixture of fuming nitric and concentrated sulfuric acids (4). The potassium salt of dinitromethane has been prepared by Villiers (3).

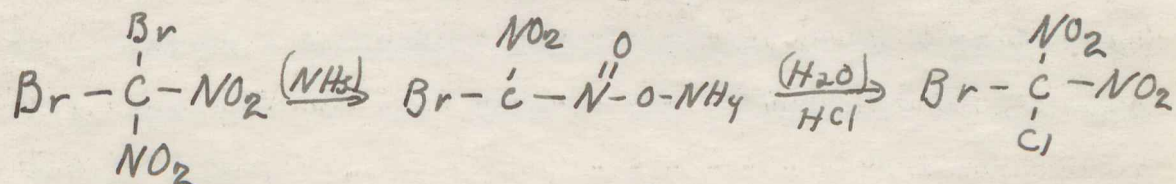
The preparation of nitroform by heating of tri-nitro acetonitrile has been recorded by Schischkow (5). Some of the higher nitroalkyls are now available commercially (6).

There is occasional reference to the halogenated nitro-methanes, mostly before 1900. Schischkow describes the preparation of bromnitroform from nitroform and bromine. (7) Dibromdinitro methane has been made in several ways; by heating symmetrical tribrom aniline with concentrated nitric acid (8), and by heating ethylene bromide (9), or bromphenol or dibrom-para-toluidine (10) with fuming nitric acid. When

the analogous reaction for the chloro compounds is tried, the yields are not as great.

Losanitsch (11) has described chlorobromo dinitromethane, which he prepared by passing chlorine into an aqueous solution of the potassium salt of bromnitroform. It is a yellow, pungent-odored, heavy oil, which decomposes on heating. It is easily soluble in alcohol, slightly soluble in water, and forms chloro dinitromethane with potassium hydroxide.

Schmidt, Sunderlin, Cole, and others have studied the formation of halogen nitromethane derivatives by direct halogenation of the ammonium salts which formed from liquid ammonia reactions (12). Cole's work with dibrom dinitro methane in liquid ammonia indicated the formation of a salt similar to that described by Losanitsch (11). Cole's description of its structure and its reaction upon chlorination are:



This method for the formation of chlorobromo dinitromethane was the one used in this work.

SYNTHESIS OF CHLOROBROMODINITROMETHANE

The starting material in the preparation was aniline.

The aniline was dissolved in dilute hydrochloric acid, so that the solution remained slightly acid. The solution of aniline hydrochloride was then brominated by passing bromine vapor into it in a stream of air, during which a flocculent white precipitate of symmetrical tri-brom aniline formed. This was filtered off with suction, washed, and dried. The dried precipitate was reacted with concentrated nitric acid (3 cc. conc. acid per gram of the precipitate). The reaction, which was carried out in a round-bottomed flask with a reflux condenser, needed heat to start, but quickly became violent, and it was necessary to cool the flask to maintain control, using an ice bath or a stream of cold water. Since bromine vapor and oxides of nitrogen are given off, the reaction is best carried out under a hood.

Steam distillation of the resulting acid mixture gave a black, heavy oil which was the crude dibrom dinitromethane. It was washed in a separatory funnel several times with dilute caustic, then with water. This is the method used by Losanitsch (8) and Cole (2).

It was further purified by vacuum distillation. The constants are:

Density 2.440 gm/cc

B. P. 72.4°C @ 16mm Hg

Index of Refraction n_D 1.5280

The dibrom dinitro methane was then reacted with liquid

ammonia in a dewar flask. The action is rapid and rather violent, and the organic salt should be added slowly from a dropping funnel. Upon evaporation of the liquid ammonia, a bright yellow, crystalline solid remains, which may be freed from excess ammonia by passing a current of air through the flask. Cole has shown this to be a mixture of ammonium bromide and ammonium bromnitroformate. Yields are high, nearly 100 per cent.

This compound, unlike the oily dibrom dinitro methane, is soluble in water. After being dissolved in distilled water, the chlorobromo compound was formed by passing washed chloring gas into the water solution. Some loss due to evaporation was noticed when the container was left open. In an attempt to eliminate this, chlorination under pressure was resorted to, but the reaction was very slow, due to formation of a thin film of the chlorinated compound, as an oil, on the surface. This oily film prevented reaction with the chloring gas, unless the vessel was continually agitated.

The chlorobromo dinitro methane, being almost insoluble, was easily separated as a pale yellow oil, yields being about 50 per cent of the theoretical amount. It was then vacuum distilled for further purification.

The physical constants for chlorobromo dinitro methane are as follows:

Molecular weight	219.4
Boiling point @ 16 mm	74.5--76°C
Density	2.394 gm/cc
Index of refraction	1.5173

It is a lachrymator, and is affected by light, decomposing and turning darker. It decomposes on heating in air at normal pressures. It is an oxidizing agent.

THE REACTION OF CHLOROBROMODINITROMETHANE WITH LIQUID AMMONIA

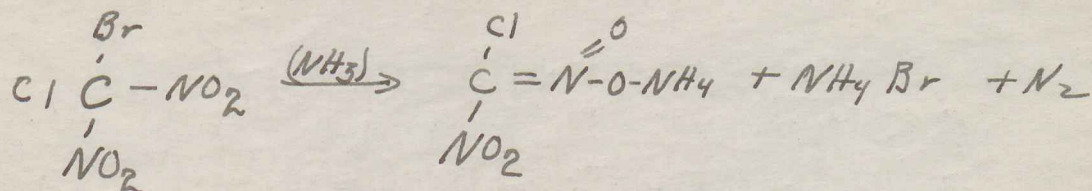
The chlorobromo dinitro methane reacts with approximately the same violence as the dibrom compound when added to liquid ammonia, and the same precautions should be observed.

Upon evaporation of the ammonia solution a yellow crystalline salt remained, very similar to the one mentioned above. This was then analyzed to determine whether the chlorine or bromine had gone. A portion was dissolved in water, made neutral to litmus, and steam distilled. The neutralization produced an oily substance which came over during the distillation. The residue was then analyzed for chloring.

The results of the chlorine analysis were negative, although a precipitate was formed with silver nitrate. This indicates that the bromine atom is the one which is removed by the reaction with liquid ammonia. This is further substantiated by the fact that the brominated nitromethanes

react almost immediately with liquid ammonia, while the reaction of the corresponding chloro compounds take several hours. Thus the bromine atom is the most reactive in liquid ammonia.

The reaction, then, is:



Thermochemical data from Lewis and Randall indicate that the bromine should be the one to go. The heats of dissociation, in kilocalories per mole, for the two bonds are:

C--Br	58 kcal
C--Cl	79 kcal

Summary

1. A method of forming nitro halogen methanes has been reported, of general application, resulting in higher yeilds than previously reported methods.

2. A bromine atom attached to a nitrated carbon atom is more reactive in liquid ammonia than the corresponding chlorine.

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