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Purdue University

Research in Polynitro Monomers and Polymers

Quarterly Report No. 2

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DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION

LAFAYETTE, INDIANA

Quarterly Report No. 2

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Compiled by:

G. B. Bachman

G. B. Bachman, Professor of Organic Chemistry

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Quarterly Report No. 2
May 12, 1953 to August 12, 1953

Office of Naval Research Fellowship No. 749
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Purdue Research Foundation and Department of Chemistry
in cooperation with

Office of Naval Research
V. Z. Pasternak, Post-doctorate Fellow
C. M. Vogt, Research Fellow
G. B. Bachman and Henry Feuer, In direct charge

Abstract

1. The complex between nitrogen tetroxide and boron trifluoride has been prepared and some of its physical and chemical properties determined. Attempts to use it as a nitrating agent in the conversion of mononitroparaffins to dinitroparaffins were unsuccessful, both in the liquid phase and at elevated temperatures in the vapor phase.

2. dl- α -Aminocaproic acid has been treated with nitrogen tetroxide in the cold and the reaction products have been isolated and characterized.

3. 1,6-Diaminohexane has been treated with nitrogen tetroxide in dry ether and also in 2-nitropropane and its reaction products have been studied.

4. Isopropylamine has been treated with nitrogen tetroxide both in dry ether and in 2-nitropropane.

5. Preliminary studies on the reaction products of 1,4-diaminobutane dihydrochloride with nitrogen tetroxide show that chlorine is present in each fraction obtained.

V. Z. Pasternak

V. Z. Pasternak

C. M. Vogt

C. M. Vogt

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8/12/53

DiscussionProperties of $\text{BF}_3 \cdot \text{N}_2\text{O}_4$ Complex

The synthesis of dinitroparaffins from nitroparaffins by the use of a new nitrating agent, $\text{BF}_3 \cdot \text{N}_2\text{O}_4$, was attempted. This complex is obtained by passing gaseous boron trifluoride through liquid nitrogen dioxide at -5°C . in a diluent of nitromethane or nitroethane. Carbon tetrachloride or chloroform may also be used as a diluent, but the final product does not appear to be pure as when a nitroparaffin is used. Oxygen and nitrogen containing compounds such as ketones, ethers, alcohols, and amines cannot be used as diluents since they react to destroy the complex and benzene cannot be used because it is nitrated by the complex at this temperature. Readily oxidized substances like aniline are definitely hypergallic with the complex.

The $\text{BF}_3 \cdot \text{N}_2\text{O}_4$ complex is a white solid which is stable if it is stored under a nitroparaffin, but will decompose if it is allowed to come into contact with any moisture. Attempts to determine the melting point of this complex were made, but no definite melting point could be found in a sealed glass capillary tube up to 265° . The complex sublimates away fairly rapidly in an open capillary tube or on an exposed surface even at room temperatures. Partial dissociation of the complex in the sealed capillary tube was indicated by the presence of brown vapors of nitrogen dioxide.

Several attempts were made to determine if this complex would function as a nitrating agent for nitroparaffins. The complex was added to nitromethane, nitroethane, and 2-nitropropane at room temperature and

allowed to stand in a stoppered flask for two weeks. There was no dinitroparaffin formed in any of these cases.

The use of higher temperatures was explored. Nitroparaffins in the vapor state along with gaseous nitrogen dioxide and boron trifluoride were introduced into a hot tube in a series of experiments. The hot tube temperature was varied from 200° to 400° while the contact time was varied from 10 to 40 seconds. In all cases, no dinitroparaffin was isolated whether nitromethane or nitroethane was used.

Experimental

Preparation of $\text{BF}_3 \cdot \text{N}_2\text{O}_4$ complex. - Gaseous nitrogen dioxide is mixed with oxygen (dried by passage through concentrated sulfuric acid) and passed through several drying towers containing anhydrous phosphorus pentoxide. The oxygen is used to oxidize any nitric oxide present to nitrogen dioxide. The dry gases are passed into a collecting tube which is kept at about -5° by an ice bath. The liquid nitrogen tetroxide is transferred to a 500 cc round bottom flask which contains an inlet for gaseous boron trifluoride and a reflux condenser. Then 200 cc. of nitroethane is added as a diluent. The reaction flask should be kept at -5° during the addition of gaseous boron trifluoride which is bubbled through the mixture at a rate fast enough to prevent the liquid from backing up into the boron trifluoride line. The reaction is complete when the dense white fumes of boron trifluoride are noticed coming off the top of the condenser. The complex may be kept in the round bottom flask under the nitroethane which is present. The flask should be stoppered to keep moisture out. The yield is essentially 100 percent and the amount of complex obtained will depend upon the weight of nitrogen tetroxide used initially.

Attempted nitration of nitroethane. - Nitroethane, 30 cc (31.5 g), was placed in a 125 ml. flask and 20 g. of $\text{BF}_3 \cdot \text{N}_2\text{O}_4$ was added. The flask was stoppered with a glass wool plug and allowed to stand for two weeks at room temperature. Then 50 cc. of water was added to destroy the complex. The organic layer was separated from the aqueous layer in a separatory funnel; the aqueous layer being discarded. The organic layer was distilled at atmospheric pressure and gave a boiling point of 115.0° . There was no higher boiling fraction obtained. The same procedure was followed with nitromethane and 2-nitropropane. Apparently no reaction occurred.

Hot tube reaction. - The liquid nitroparaffin was vaporized in a 1000 cc round bottom flask which contained a lead to the hot tube. Gaseous nitrogen dioxide was mixed with the hot vapors of the nitroparaffin and passed into the hot tube. Just before entering the hot tube, boron trifluoride was introduced into the mixture. Upon emerging from the reaction vessel, the hot vapors were run through a steam condenser and finally into a 500 cc. round bottom flask fitted with an exhaust valve. This flask was kept in an ice bath to condense the vapors. The material collected was chilled in dry ice for 15 minutes, filtered by suction to remove the complex ($\text{BF}_3 \cdot \text{N}_2\text{O}_4$), and distilled under atmospheric pressure. Several runs were made with nitromethane and with nitroethane. Starting material was recovered in all cases.

Future Work

The use of this $\text{BF}_3 \cdot \text{N}_2\text{O}_4$ complex as a nitrating and as an oxidizing agent will be tested. A melting point determination will also be tried at higher temperatures.

Reactions of N_2O_4 with Amines. - As was mentioned in the first quarterly report on this contract yellow needles, m.p. 90° (from water), were obtained from the steam distillate of the crude reaction product of dl- α -aminocaproic acid with nitrogen tetroxide when trimethylbenzylammonium hydroxide was added. This yellow salt upon analysis gave the following results: Found: C, 50.35; H, 6.42; N, 16.35.

Since the above percentages correspond to the trimethylbenzylammonium salt of a trinitropentane, the reaction by which it was formed becomes definitely valuable from a preparative standpoint.

In an effort to improve the yield of the trinitropentane and also to isolate and purify the other reaction products obtained in the reaction of nitrogen tetroxide with dl- α -aminocaproic acid the following scheme was used.

1. The volatile material was removed at the water pump at room temperature.
2. The residue, in a flask, was immersed in dry ice for several hours and then filtered immediately. A compound (A) was obtained which was in the form of colorless plates melting sharply at 99° . It was soluble in water and ether, but insoluble in petroleum ether, and gave a negative test for nitrogen.
3. The filtrate from step 2 was then titrated roughly to pH 6 with trimethylbenzylammonium hydroxide solution using external cooling. The dark red heterogeneous substance was allowed to stand overnight.
4. The above mixture was then shaken with 3-4 portions of petroleum ether (b.p. $90-100^\circ$). The petroleum ether phase was further purified by filtering through Norit A. After the removal of petroleum ether an almost colorless viscous substance, fraction (B), was obtained. It was heavier than and insoluble in water, but soluble in ether, petroleum ether and strong alkali.

5. The cloudy aqueous solution was passed through activated Norit A. After the Norit was washed with water and a small volume of methanol, the salt was eluted with acetone giving a yellow clear solution. The acetone was removed at room temperature at the water pump and the residue, compound (C), was crystallized from water, m.p. 88°.

A small portion of the crude reaction product was brought to pH 6, by the use of potassium carbonate and subjected to the same treatment as the trimethylbenzylammonium salt solution, but the potassium salt did not seem to be adsorbed by the Norit.

It was noticed that when the ratio of dry purified nitrogen tetroxide was high, i.e. over tenfold that of the amino acid, the crystalline salt with trimethylbenzylammonium ion was not obtained. To find the optimum ratio of reactants and the optimum conditions for the reaction the previously described procedure was slightly varied.

Ten grams of dl- α -aminocaproic acid was treated with 55 ml. of purified dry nitrogen tetroxide at -5° and kept for 70 hours at -5 to -3° and then exposed to room temperature. As soon as the reaction flask was removed from the cold bath the large colorless crystals present began to decompose vigorously. After the removal of the excess nitrogen tetroxide at room temperature 14 ml. of a light yellow liquid was obtained.

Since the amino group of an amine reacts far more vigorously with nitrogen tetroxide than the α -amino group of an amino acid, the reaction with amines was run at a much lower temperature and also in a solvent such as dry ether or a nitroalkane.

An ether solution of 1,6-diaminohexane, b.p. 90°/12mm (5 g. in 200 ml of ether) was added dropwise to 90 ml. of nitrogen tetroxide in 200 ml of dry ether in a dry ice bath. After completion of the addition, the reaction flask was transferred to a salt-ice bath and kept there for

48 hours. The solid reaction intermediate disappeared after a few days. The subsequent decomposition at room temperature was accompanied by gas evolutions and was carried out with extreme caution. The temperature of the reaction mixture was controlled as necessary by immersing the reaction flask in ice cold water.

After the removal of volatile material at the water pump a small portion of the reaction product was dissolved in chloroform and crystals melting at 92° were obtained. These were recrystallized from water to m.p. 180°. They gave a negative test for nitrogen. More of these colorless crystals melting at 180° were obtained by deep freezing the crude reaction product. The trimethylbenzylammonium salt of the viscous, heavy filtrate melted at 143°. An analysis of these has not yet been obtained.

When 1,6-diaminohexane was reacted with nitrogen tetroxide in 2-nitropropane instead of ether, the only experimental difference was that in lieu of a clear solution of the amine in ether, the solid salt of diaminohexane with 2-nitropropane was added to a solution of nitrogen tetroxide in 2-nitropropane. On deep freezing the reaction product, the same colorless substance melting at 180° was obtained. The filtrate was converted to the trimethylbenzylammonium salt which is in the process of being studied.

Isopropylamine, b.p. 33-35°, was treated with nitrogen tetroxide both in dry ether and in 2-nitropropane in the usual way. There was no visible difference between the two solvents since there was no precipitate formed when isopropylamine was dissolved in 2-nitropropane. The crude reaction product from the ether run gave a crystalline purplish salt, m.p. 125° with trimethylbenzylammonium hydroxide solution. At the time hardly any attention was paid to these well-defined violet plates since the expected product was the neutral 2,2-dinitropropane. The second solid substance obtained from the reaction product was a colorless crystalline

compound which lost its crystalline form at about 90° and melted with decomposition at 175-180°. The reaction product from the nitropropane run has not been identified as yet.

1,4-Diaminobutane dihydrochloride was reacted with N_2O_4 in ether. Two colorless crystalline products and a yellow liquid were obtained after working up the crude product. The compound melting at 115° seems to contain both chlorine and nitrogen while the compound melting at 175° contains chlorine but no nitrogen. The yellow liquid will be further investigated.

Future Work

1. Optimum conditions and the limitations of the reaction between the $-NH_2-$ group and the N_2O_4 will be further established.
2. The different reaction products will be studied and identified.

N7onr-39417

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