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OSRD No. 334
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Section B-2

The Preparation of Tetranitromethane (OD-11)

by Charles D. Hurd

OSRD No. 334

Serial No. 164

January 20, 1942

Endorsement (1) from Frank C. Whitmore, Chairman, Section B-2 to Roger Adams, Chairman, Division B. Forwarding report and noting:

> "The preparation of tetranitromethane from acetylene and nitric acid, from acetic anhydride and nitrogen pentoxide, and from acetic anhydride and nitric acid was investigated. The most satisfactory method was the last which gave yields of 60-66%. The action of nitric acid on six compounds containing the CH_3CO- group and on ketene yielded no tetranitromethane."

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Report on "Preparation of Tetranitromethane"

by
Dr. C. D. Hurd, Professor of Organic Chemistry
at Northwestern University

OSRD No. 334

Serial No. 164

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Date: January 20, 1942

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CH_3CO-

(2) Twenty-three copies forwarded to Dr. Irvin Stewart, Secretary of the National Defense Research Committee, as Progress Report under Contract B-11, NDCrc-7 (supplement #1) with Northwestern University.

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PREPARATION ON TETRANITROMETHANE

By

Charles D. Hurd

ABSTRACT

Of the many preparations of TNM described in the literature[1], the only ones deemed of sufficient interest to be investigated were;: 1) the action of nitric acid on acetic anhydride, 2) the action of nitric acid on acetylene, 3) the action of nitrogen pentoxide on acetic anhydride. It was also thought desirable to attempt the preparation by: 1) the action of fuming nitric acid on various organic compounds, particularly those containing the group CH_3CO-, 2) the vapor phase nitration of various organic compounds, 3) the action of nitrogen pentoxide on ketene.

Of these methods, the reaction between acetic anhydride and nitric acid seems the most promising. The reaction is best carried out in all-glass equipment consisting of a flask, mechanical stirrer, dropping funnel, thermometer and condenser. Commercial fuming nitric acid can be used but the yield of TNM is higher if the nitric acid is purified by vacuum distillation. No advantage is gained in purifying the acetic anhydride. The optimum temperature of reaction is 20-25°C and the yield is enhanced by the presence of chipped glass. The yields of a considerable number of experiments average 61 to 62 per cent.

DISCUSSION

Action of Nitric Acid on Acetic Anhydride. Chattaway has suggested the following equation for the reaction:

$$4\ (CH_3CO)_2O + 4\ HNO_3 \dashrightarrow 7\ CH_3COOH + C(NO_2)_4 + CO_2$$

The various methods suggested for carrying out this reaction involve differences in the reaction temperature during mixing, the use of a diluent, the concentration of the nitric acid used, the ratio of the reactants, the presence of particles of glass, the use of catalysts, the length of time allowed for completion of the reaction and the temperature during the period of standing. A series of experiments was carried out to determine the effects of some of the above variables on the yield of TNM.

Different concentrations of nitric acid were used varying from ordinary concentrated acid (70%) to colorless nitric acid of high concentration. In general, it appeared that the more highly concentrated and purified the acid the higher the yield of TNM. Seventy per cent nitric acid yielded no TNM; fuming technical acid yielded on the average about 30% TNM; fuming C.P. acid although less concentrated than the fuming technical acid yielded 35 to 40% TNM; and colorless fuming acid yielded 53 to 58% of the theoretical amount of TNM. Subsequent experiments with colorless fuming acid donated by the Navy yielded 61-62% of the theoretical amount of TNM.

The acetic anhydride and nitric acid were used in roughly equivalent amounts, but a slight advantage was noted by having the anhydride in slight excess.

The temperature of reaction during mixing of the nitric acid and the acetic anhydride should be kept at 20 to 25°C since higher temperatures resulted in vigorous evolution of nitrogen dioxide (and carbon dioxide?) with consequent lowering of yields. Similarly the temperature at which the reaction stands after completion of the addition should be 20-25°C. At this temperature, the reactions were substantially complete after 8 or 10 days.

The advantage in the use of sharp angular particles as recommended in Wyler's patent, was clearly shown by the increased yields of TNM when small amounts of chipped glass were added to the reaction vessel. However, the advantages he claims for the addition of small amounts of phosphorus pentoxide, sulfuryl chloride and sulfuric acid could not be substantiated. The addition of ketene was found to be deterimental to the yield. Purification of the acetic anhydride did not enhance the yields of TNM.

Diluents had no beneficial effects except to facilitate temperature control.

The Action of Nitric Acid On Acetylene.

A few trial runs indicated that TNM can be prepared by this reaction but rigid control is necessary for optimum results. At best, the yields were poor based on the nitric acid, which was used in large excess. The cost of this method would be prohibitive compared to the more efficient production from acetic anhydride even if the nitric acid were recovered.

The Action Of Nitrogen Pentoxide On Acetic Anhydride The optimum yields (47% based on nitric acid) were obtained by using nitrogen pentoxide prepared by distilling colorless nitric acid from phosphorus pentoxide. Nitric acid heavily fortified with nitrogen pentoxide is better for this reaction than nitrogen pentoxide alone.

Various Unsuccessful Methods 1.) It was thought that various compounds containing the group CH_3CO- might be used in place of acetic anhydride to produce TNM. However, treatment of acetone, acetonitrile, ethyl acetate, acetamide, glacial acetic acid, or nitroacetic-acetic anhydride failed to yield any TNM when nitrated under the same conditions which were successful for acetic anhydride. (2.) It was also found that ketene could not replace acetic anhydride in these nitrations, in fact, ketene inhibited the normal reaction with acetic anhydride. Likewise ketene reacting with nitrogen pentoxide failed to yield any TNM. (3) A series of experiments in which ethylene, acetylene, acetic anhydride or ketene was passed, together with 70% nitric acid, through a glass tube heated at 300°C. failed to yield any TNM.

Experimental Part

Materials

Acetic Acid, Glacial (Grasselli).
Acetylene, from high pressure cylinder.
Acetic Anhydride, commercial grade (Carbide & Carbon).
Acetic Anhydride, purified. The commercial grade of acetic anhydride contained acetic acid, so it was treated with ketene and distilled through an efficient column.
Ketene, generated at the rate of 0.4 mole per hour by the pyrolysis of acetone, using the apparatus of Williams and Hurd (J. Org. Chem. 5. 122 (1940).
Nitric Acid, 70%, d 1.42 (Baker).
Nitric Acid, Fuming, technical grade, d. 1.52 (Baker). Its color was brownish-red.
Nitric Acid, Fuming C. P. (Baker's Analyzed), d.1.49-1.50, assay 89-95% HNO_3. It was a light yellow color.
Nitric Acid, colorless, d. 1.52-1.53, 1) produced by vacuum distillation (20mm.) of a mixture of equal volumes of nitric (fuming, C. P. or technical) acid and concentrated sulfuric acid, using all-glass equipment. 2) donated by the Navy.

The Action of Nitric Acid on Acetic Anhydride Three hundred c. c. of ice-cold colorless fuming nitric acid is placed in a flask carrying a stirrer, thermometer, condenser, dropping funnel and glass chips, and 650 c.c. of commercial acetic anhydride is slowly added, while maintaining the temperature at 15-20°. After standing at 25° for thirteen days 3 l. of water is added and the insoluble layer separated. The aqueous layer is then steam distilled and the non-aqueous phase obtained is added to the main portion drawn off of the crude reaction mixture. (Steam distillation of the entire crude mixture leads to considerable loss of TNM due to nitroform formation by reaction with hot water). The crude product is washed with 5% sodium bicarbonate, then with water and dried over anhydrous sodium sulfate. The yield of TNM is 209g (61.8% of the theoretical).

This procedure was repeated, except that after eight days of standing at 25°, 100 cc. of acetic anhydride and approximately 4 g. of phosphorus pentoxide were added. After standing for eight additional days, 230 g. of TNM (66% of theoretical) was isolated by the usual method.

The Action of Nitric Acid on Acetylene Approximately 10 l. of acetylene is passed at room temperature through a Sargent gas bottle containing 134 c.c. (200 g.) of technical fuming nitric acid and 1.2 g. of mercuric nitrate. After completion of the gas passage, 300 c.c. of sulfuric acid (d 1.84) is added, the resulting mixture heated slowly to about 80° and again cooled. One thousand c.c. of cracked ice is added and after standing in a cool place over night, 10.0 g. of TNM is isolated in the usual way. This is about 7% of the theoretical based on the nitric acid used.

The Action Of Nitrogen Pentoxide On Acetic Anhydride One hundred c. c. of colorless nitric acid and 30 g. of phosphorous pentoxide are distilled at 25 mm. pressure to yield 105.5 g. of material which is almost pure nitrogen pentoxide (d. 1.61 at 9°C.). This heavily fortified nitric acid is treated with 270 c.c. of commercial acetic anhydride in the apparatus and under the conditions of the experiment described above for the reaction of nitric acid and acetic anhydride. After standing over night, the mixture was heated to 40°C. for 1½ hours, and after standing for 7 days at 20°, 54.5 g. (46.6% of the theoretical) of TNM is isolated in the usual way. This experiment using 100% nitrogen pentoxide leads to much lower yields.

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