amide. The product may be recrystallized from ethanol. Before recrystallization, it is desirable to elute the crude product with ethanol saturated with methylenediformamide from previous recrystallizations. Decolorizing charcoal is used to remove colored material when necessary. Methylenediformamide melts at 142–143°.

B.—The formamide mother liquor (from A in the first pass or B in the later passes) is treated with Darco G60 to decolorize it, and then it is combined with the wash formamide (90 g.) and 23 g. (0.167 mole) of hexamethylenetetramine and the above procedure is repeated. The yields of crude product from a typical series of runs are recorded in Table I.

TABLE I

METHYLENEDIFORMAMIDE FROM HEXAMETHYLENETETRAMINE WITH 100% EXCESS FORMAMIDE

Run	Mother liquor from run	Hexamine, mole	Formamide, moles	Yield, G.	Yield, %	Total yield G.	Total yield %
1		0.5	12	162	53	162	53
2	1	.167	2	124	121	286	70
3	2	.167	2	108	106	394	77
4	3	.167	2	97	95	491	80
5	4	.167	2	95	93	586	82
6	5	.167	2	95	93	681	83

Methylenediacetamide.—This compound was prepared from acetamide and hexamethylenetetramine in the same manner as methylenediformamide using quinoline as solvent. The product, melting at 198–200° after recrystallization from isopropyl alcohol, did not depress the melting point of an authentic sample of methylenediacetamide.

Methylenebis-(malonamide).—This compound was prepared from malonamide and hexamethylenetetramine in refluxing dimethylformamide. The yield of product, melting at 252° dec. after recrystallization from 90% formic acid or from formamide, was 82.5%.

Anal. Calcd. for $C_7H_{12}O_4N_4$: C, 38.89; H, 5.59; N, 25.92. Found: C, 39.12, 38.90; H, 5.72, 5.50; N, 25.55, 25.73.

Methylenedibenzamide.—This compound was prepared from benzamide and hexamethylenetetramine in refluxing quinoline. The product, melting at 216–220° after recrystallization from isopropyl alcohol, did not depress the melting point of an authentic sample of methylenedibenzamide.

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Nitramines. I. Methylenedinitramine[1]

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Recently it became necessary to prepare a quantity of methylenedinitramine. This compound has been prepared previously from hydrolysis of 1,3-dinitro-1,3,5-triazacyclohexane 5-nitrate with barium hydroxide and isolation through its barium salt, and also from methylenediacetamide by nitration to methylenedi-(nitroacetamide) followed by hydrolysis.[2]

Since the formyl group has been found very useful where a labile protecting group is desired, as in the synthesis of amino acids, the use of methylenediformamide instead of methylenediacetamide for the synthesis of this compound was investigated. Nitration of a suspension of methylenediformamide (MDF)[3] in acetic anhydride by anhydrous nitric acid produced methylenedi-(nitroformamide), which on hydrolysis gave methylenedinitramine in nearly quantitative yield.

Since this new procedure gave substantially superior yields to previous methods for the preparation of nitramines, variables influencing yield have been investigated. The use of this reaction for the preparation of other nitramines also is being investigated and will be reported later.

In initial work on the nitration process, all of our studies were made using a 9/4/1 ratio[4,5] of anhydrous nitric acid to acetic anhydride to methylenediformamide, with a nitration and aging temperature of 0°. The yield of methylenedi-(nitroformamide) was found to increase with aging time until a nearly quantitative yield was obtained with a four-hour aging period.

Table I shows the influence of increased nitration temperature on the yield of crude methylenedinitramine. A study of various nitrating mixtures showed that no methylenedi-(nitroformamide) was obtained using nitric acid alone or in mixture with sulfuric acid, which is similar to the finding of Brian and Lamberton[4] for the nitration of methylenediacetamide. With acetic anhydride–nitric acid mixtures, decreasing amounts of nitroamide were obtained when the amount of water in the nitric acid used was increased; this, however, could be overcome by the pre-addition of enough anhydride to the acid to react with the water present. Any decrease in the ratio of acetic anhydride or nitric acid to methylenediformamide, or the substitution of ammonium nitrate for a portion of the nitric acid, was found to cause a decrease in the yield of methylenedinitramine. However, when trifluoroacetic anhydride was substituted for acetic anhydride, the ratio of acid to anhydride to methylenediformamide could be reduced to 3/3/1 to obtain a quantitative yield. No decrease in yield was obtained with acetic anhydride–nitric acid mixtures when the order of addition was changed. Contrary to

TABLE I

INFLUENCE OF NITRATION TEMPERATURE WITH TIME ON YIELD OF METHYLENEDINITRAMINE

Mole of MDF	Nitration[a] temp., °C.	Aging temp., °C.	Aging time, hr.	Crude yield, %
1	0	2	4	95
0.5	10	10	1	97
0.5	10	10	2	100
0.5	10	10	4	93
1	25–30	15–30	3	99

[a] An acid/anhydride/MDF ratio of 9/4/1 was used. Formic acid was added for the hydrolysis, and the methylenedinitramine was isolated by azeotropic distillation with xylene at reduced pressure.

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[1] This work was done under Contracts DA-19-020-ORD-12 and DA-19-020-ORD-47 with the Office of the Chief of Ordnance and has been released for publication by the Office of Public Information, Department of Defense.

[2] A. H. Lamberton, *Quart. Revs.*, **5**, 75 (1951).

[3] P. Knudsen, *Ber.*, **47**, 2699 (1914); C. W. Sauer and R. J. Bruni, THIS JOURNAL, **77**, 2259 (1955).

[4] R. C. Brian and A. H. Lamberton, *J. Chem. Soc.*, 1635 (1949).

[5] Heat of reaction data for the nitration reaction were calculated by Dr. G. R. Handrick, Arthur D. Little, Inc., from heat of combustion data obtained by a new method which will be given in detail in a forthcoming publication. $CH_2(NHCHO)_2 + 4(CH_3O)_2O + 9HNO_3 \rightarrow CH_2(N(NO_2)CHO)_2 + 6CH_3COOH + 5HNO_3 + 2CH_2C(O)ONO_2 +$ 30.4 kcal./mole (heat evolved). The heat evolved on nitration was determined experimentally by Dr. J. W. Lawrence, Atlas Powder Co., as 29.5 kcal./mole.

work reported elsewhere,[6] the use of red fuming nitric acid containing urea instead of anhydrous nitric acid gave very low yields of methylenedi-(nitroformamide).

The facile spontaneous hydrolysis of methylenedi-(nitroformamide), even at room temperature, prompted us to investigate the acid hydrolysis of the compound. Calculation of the heat of hydrolysis in the same manner as the heat of nitration[5] shows the evolution of 12 kcal./mole for this reaction. Hydrolysis was investigated in various media including methanol, isopropyl alcohol, water, 2 *N* hydrochloric acid, concentrated hydrochloric acid, 90% formic acid and glacial acetic acid. As methylenedinitramine is most stable in solutions of low *p*H,[4] the best yields are obtained using an acidic medium (methylenedinitramine is unstable in sulfuric acid). The product is contaminated with polymeric solids when hydrolysis takes place in very concentrated solution at *p*H 3-6.

A study of the thermal decomposition of methylenedinitramine has been made and is reported elsewhere.[7]

Experimental

Methylenedi-(nitroformamide).—Absolute nitric acid (19 ml., 0.45 mole) was added at 10–15° dropwise with stirring to a suspension of methylenediformamide (5 g., 0.05 mole) in 19 ml. of acetic anhydride (0.2 mole). The resulting solution was aged for 2 hours at ice temperature and then run into 150 ml. of ice and water with stirring. The precipitate was collected and washed several times by slurrying with ice-water. The product was pressed dry on the filter and then dissolved in 30 ml. of ethyl acetate. The solution was separated from the adhering water and dried over anhydrous sodium sulfate. The ethyl acetate solution was concentrated *in vacuo* to the formation of a precipitate, 10 ml. of isopropyl alcohol was added and the product was collected. The nitroformamide was recrystallized twice by dissolving in 3 ml. of acetone, diluting with 6 ml. of isopropyl alcohol, and then adding 10 ml. of Skellysolve B (it also may be recrystallized from boiling ethylene chloride). The purified product melted at 87–87.5°.

Anal. Calcd. for $C_2H_4O_6N_4$: C, 18.75; H, 2.10. Found: C, 18.76; H, 2.34.

Methylenedinitramine.—Absolute nitric acid (380 ml., 9 moles) was added as rapidly as possible at ±2° (Dry Ice–kerosene cooling) to a well-stirred suspension of 102 g. (1 mole) of methylenediformamide (m.p. 142–143°) in 380 ml. (4 moles) of acetic anhydride. Upon completion of the nitric acid addition, the Dry Ice–kerosene-bath was removed and replaced by an ice-bath, and the mixture allowed to age with ice-cooling for 4 hours. After application of the ice-bath, the temperature of the reaction mixture rose to 8° during 0.25 to 0.5 hour and then fell to +2°, where it remained during the remainder of the aging period. At the end of the aging period, the reaction mixture was run in a stream during 5 minutes into a well-stirred mixture of 500 ml. of water and 1500 g. of finely crushed ice. The precipitate of methylenedi-(nitroformamide) was immediately[8] collected on a filter and washed with three 100-ml. portions of ice-water. The filter cake was pressed dry by use of a rubber dam. The yield at this point was 200 to 300 g. of damp material. The methylenedi-(nitroformamide) was stirred into 105 ml. of 90% formic acid[9] and the resultant paste allowed to hydrolyze[10] by standing overnight. The formic acid and water were removed from the methylenedinitramine by codistillation with xylene.

The recycling xylene azeotropic distillation of formic acid and water was carried out at 25–35° (10–15 mm.) until 1 hour after liquid had ceased to separate from the condensing xylene and the methylenedinitramine had crystallized as a sand. The crude methylenedinitramine[11] was collected on a filter and dried at reduced pressure over paraffin and sodium hydroxide. The yield of material melting at 98–103° was 80–100% based on methylenediformamide.

The crude methylenedinitramine was purified by recrystallization from 2-nitropropane (3 ml./g. at 70–75°) or 9/1 mixture (by volume) of ethylene dichloride and isopropyl alcohol (5 ml./g.). The latter solvent returns 80% in the first crop of crystals. Purified methylenedinitramine melts at 105–106° and decomposes when heated above 110°.

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[6] Private communication from Dr. John Dawson, Rohm and Haas Co.

[7] M. C. Tobin, J. P. Fowler, H. A. Hoffman and C. W. Sauer, This Journal, **76**, 3249 (1954).

[8] Isolation of the methylenedi-(nitroformamide) by precipitation from the reaction mixture in a mixture of ice and water is a very critical point in the procedure. If the temperature of the precipitating solution is allowed to rise above 0°, hydrolysis will take place along with the precipitation and no product will be isolated. This ease of hydrolysis also necessitates rapid separation of the material from the drowning mother liquor, as the yield decreases to less than half on standing for 15 minutes prior to filtration.

[9] An alternate procedure for the hydrolysis of the methylenedi-(nitroformamide) was the following: After the precipitated methylenedi-(nitroformamide) had been collected on the filter, it was washed with three 50–100 ml. portions of ice-cold 2 *N* hydrochloric acid. The dry filter cake (15–25% water) was allowed to hydrolyze without addition of further reagents. The methylenedinitramine was isolated from this hydrolysis solution by either crystallization at −30° or by vacuum azeotropic distillation with xylene.

[10] Hydrolysis of methylenedi-(nitroformamide) produces a solution of methylenedinitramine in the formic acid formed by hydrolysis together with any solvent which had been added. Crystalline methylenedinitramine can best be isolated from this solution either by removal of the solvent (azeotropic distillation) or by low temperature crystallization. Extraction merely gives a second solution from which the compound must still be isolated. Low temperature crystallization was satisfactory when concentrated hydrochloric acid, formic acid, acetic acid, and no solvent other than adherent wash water (2 *N* hydrochloric acid) were used for the hydrolysis.

[11] An alternate procedure for the isolation of methylenedinitramine from the hydrolysis solution was the following: After filtration through acid-hardened filter paper to remove dirt and other insoluble material, the hydrolysis solution was allowed to stand at −30° with intermittent stirring for 8–24 hours. The crystalline methylenedinitramine was collected on a filter and dried *in vacuo* over paraffin and sodium hydroxide. The yield was 62–79% when no solvent was added for hydrolysis and 50–55% when 90% formic acid was added for hydrolysis. Additional methylenedinitramine (20–30%) was obtained from the mother liquor by concentration *in vacuo* to one-quarter volume followed by crystallization at −30°.

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Removal of Peroxides from Ethers with Cerous Hydroxide

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In order to obtain readily pure sodium iodide by recrystallization from aqueous solution at room temperature *p*-dioxane has been used to lower the solubility of this salt. Prior to its use for this purpose it is necessary to remove the peroxide found present (*via* the iodide test) in the best grades of *p*-dioxane commercially available. The different methods commonly employed for removing peroxides from ethers were considered and found to have certain undesirable physical or/and chemical features.

It has long been known that cerous hydroxide, an insoluble white solid with somewhat the same texture as ferric hydroxide when precipitated from aqueous solution, reacts quantitatively and readily with hydrogen peroxide in very dilute aqueous solution.[1] This property has been found very useful

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[1] T. Cléve, *Bull. soc. chim.*, **43**, 53 (1885).