$C_{16}H_{26}O_6$: C, 61.2; H, 8.28; CH_3O, 9.88; mol. wt., 314. Found: C, 61.2; H, 8.44; CH_3O, 10.0; mol. wt., 304.[20]

Cleavage of L′-(L-Menthoxy)-D-carbomethoxy-diglycolic Aldehyde.—A 1% solution of the dialdehyde in 90/10 methanol–water was heated under reflux at 70° for one-half hour in the presence of twice the quantity of semicarbazide hydrochloride needed to react with four carbonyl groups (two already present, two formed on hydrolysis). During the heating a heavy white precipitate appeared and was removed at the end of the reaction period by centrifugation, and washed twice with hot 90% methanol. Since this compound was insoluble in all organic solvents and water it could not be recrystallized. It was, however, found to be soluble in cold 3 *N* NaOH. After filtering the alkaline solution, the compound was precipitated by acidification with cold 6 *N* H_2SO_4. It was then washed neutral and dried *in vacuo* over $CaCl_2$; m.p. 273°, m.p. mixed with known glyoxal disemicarbazone, 273°. During the early attempts to prepare derivatives of the parent dialdehyde numerous derivatives of glyoxal resulted, all melting at the correct temperatures, alone and mixed with authentic derivatives of glyoxal. Hence the two-carbon moiety is glyoxal and represents carbon 1 and 2 of the original glucuronic acid; yield 75–90%.

The supernatant liquid left after the removal of the glyoxal derivative was evaporated *in vacuo* to a small volume and extracted with ether. The ether extract was evaporated to dryness leaving a white crystalline solid having the appearance and odor of menthol. This residue was treated with 3,5-dinitrobenzoyl chloride, yielding a crystalline derivative melting at 153°; m.p. mixed with known menthyl 3,5-dinitrobenzoate, 152°. Hence the dialdehyde contains the menthyl group. This step is not a part of the dehydration, but serves only to identify the menthol moiety.

The aqueous solution left after ether extraction was chilled several hours, yielding a cream-colored precipitate, which was readily recrystallized from 50% methanol, washed twice with cold water, and dried *in vacuo* over $CaCl_2$; m.p. 215°. *Anal.* Calcd. for $C_6H_{10}O_4N_6$: C, 31.3; H, 4.35; N, 36.5; CH_3O, 13.5. Found: C, 31.31; H, 4.42; N, 36.47; CH_3O, 13.47. Hence the compound is the disemicarbazone of mesoxalaldehyde methyl ester and represents carbons 4, 5 and 6 of the original glucuronic acid; yield 40–50%.

Determination of Periodic Acid.—HIO_4 was determined iodometrically by the procedure described by Jackson.[21]

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[20] Cryoscopic in Exaltone.

[21] E. L. Jackson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, 1944, p. 361.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEW HAMPSHIRE]

The Nitration of Melamine and of Triacetylmelamine[1]

BY EDWARD R. ATKINSON

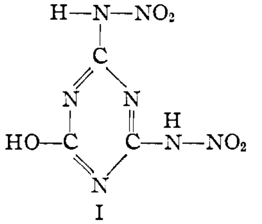
The substance $C_3H_3O_5N_7$ which Cason[3] obtained by the nitration of melamine in acetic anhydride has been identified as N,N′-dinitroammeline (I). The substance "TM-1" ($C_9H_9O_{12}N_{15}$) which Cason obtained by the nitration of triacetylmelamine in acetic anhydride has been identified as nitroammelide ($C_3H_3O_4N_5$) (II) and its hydrolysis product "TM-2" ($C_9H_9O_9N_9$) as cyanuric acid ($C_3H_3O_3N_3$) (III). Fuming nitric acid alone at 25° converted triacetylmelamine to N-nitro-N′,N″-diacetylmelamine (IV).

While examining synthetic routes to *sym*-trinitromelamine we have had occasion to repeat earlier work of Whitmore[2] and of Cason,[3] who studied the direct nitration of melamine, and of Cason[3] who studied the nitration of *sym*-triacetylmelamine.

By the nitration of melamine with nitric acid in acetic anhydride at 5° we have obtained the explosive substance $C_3H_3O_5N_7$ for which Cason offered no structural formula. We have observed that the substance can be titrated as a dibasic acid and that it is hydrolyzed quantitatively to cyanuric acid. It is clear that the substance must be N,N′-dinitroammeline (I).

By the nitration of *sym*-triacetylmelamine with nitric acid in acetic anhydride at 20–25° Cason obtained a substance designated TM-1 to which he assigned the formula $C_9H_9O_{12}N_{15}$. This was observed to hydrolyze with the loss of three molecules of nitrous oxide to form a very stable substance, TM-2, $C_9H_9O_9N_9$. In repeating this work we have noted that the substance TM-2 is cyanuric acid, $C_3H_3O_3N_3$ (III). It is apparent that the substance TM-1 is nitroammelide, $C_3H_3O_4N_5$ (II). On the basis of this formula one mole of nitrous oxide is liberated during hydrolysis.

We have made the additional observation that fuming nitric acid alone at 20–25° converts triacetylmelamine to N-nitro-N′,N″-diacetylmelamine (IV).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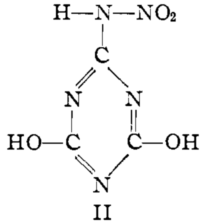
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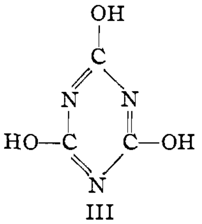
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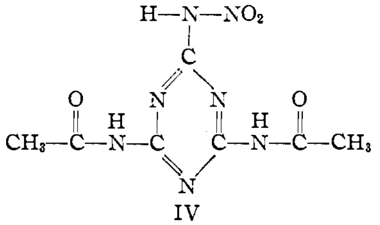
IV

Because of the large volumes of nitrating agent required in these reactions it is apparent that there is ample water (or its solvolytic equivalent) to account for the observed loss of exocyclic nitrogen atoms and acetyl groups. The hydrolysis of the nitration products with loss of nitrous oxide is typical of nitramines.[4]

Experimental Part

Nitration of Melamine.—Commercial Monsanto melamine was purified by a procedure similar to that of Salley

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[1] This work is based on work done for the Department of the Army under Contract DA19-020-ORD-12 with Arthur D. Little, Inc.

[2] Work carried out at Pennsylvania State College under the direction of F. C. Whitmore under a contract with the Office of Scientific Research and Development (OSRD Report 351).

[3] James Cason, THIS JOURNAL, **69**, 495 (1947).

[4] Lambertson, Lindley and Speakman, *J. Chem. Soc.*, 1650 (1949).

and Gray.[5] A 10-g. sample was nitrated as described by Cason[3]; smaller volumes of nitrating agent, reaction temperatures of 15° and reaction times of less than two hours led to diminished yields. We observed that crystallization of the sodium salt as a purification method could be avoided by dissolving the washed crude in 200 cc. of 10% sodium bicarbonate and filtering by suction after one minute, with use of a filter aid. This process permitted the removal of the major portion of a less acidic by-product which dissolved quite slowly. Before discarding the insoluble material it was washed on the filter with water to dissolve any sodium salt of dinitroammeline which was sometimes present.

The filtrate and washings were cooled to 0° and acidified with 6 *N* hydrochloric acid to *p*H 5–7, then filtered to remove any less acidic by-product which appeared as a flocculent solid. The filtrate was then further acidified while shaking to precipitate a granular solid which was dried at 40° overnight. There was obtained 7.5–8.9 g. (44–52% yield) of dinitroammeline.

Anal. Calcd. for $C_3H_3O_5N_7$: C, 16.58; H, 1.39; N, 45.2. Found: C, 16.7, 16.7; H, 1.32, 1.52; N, 45.3, 45.5.

Material identical with the above was obtained by acidification of the purified sodium salt as described by Cason. We observed that the yields of dinitroammeline were not affected by the presence of either acetyl chloride or zinc chloride during the nitration step. This is in accord with Wright's thesis[6] that chloride catalysis is without effect in the nitration of weakly basic amino groups.

Pure dinitroammeline decomposes sharply without melting at 228°; it can be detonated by a sharp blow. The heat of combustion, determined at Picatinny Arsenal, is 1673 cal./g. When an electrometric titration with 0.1 *N* sodium hydroxide was performed a two-step curve was obtained. The end-point of the second step corresponded to a neutralization equivalent of 104; (calcd. for $C_3H_3O_5N_7$ as a dibasic acid, 108.5). The substance hydrolyzed rapidly at 80° with liberation of nitrous oxide; quantitative yields of cyanuric acid were obtained. The hydrolysis required one or two days at room temperature; it was catalyzed by acid.

Because of the importance of the identification of cyanuric acid in this and the following section it was observed that the material obtained by us was identical with an authentic specimen in the following particulars: (a) the solid was easily crystallized from hot water and obtained as stout needles which effloresced completely at room temperature; (b) the solid sublimed rapidly and completely when heated on a spatula, with the evolution of the typical cyanic odor; (c) the solid gave excellent values for the neutralization equivalent as a monobasic acid; (d) the solid dissolved very slowly in 5% sodium bicarbonate solution at room temperature but dissolved rapidly when warmed. Analytical data for the substance and its salts has been given by Cason.[3]

Nitration of Triacetylmelamine.—Triacetylmelamine was prepared as described previously.[3] Conversion to the hydrate by water at room temperature was observed. Nitration at 25° and isolation of the product was performed as described by Cason.

Cason's "TM-1" which we designate as nitroammelide decomposes sharply without melting at 248°. We were able to recover it from concentrated solutions of its stable sodium salt by acidification. It was also sublimed slowly without decomposition at 200° and 1 mm.

Anal. Calcd. for $C_3H_3O_4N_5$: C, 20.82; H, 1.76; N, 40.5. Found: C, 21.2; H, 2.43; N, 41.2.

Quantitative hydrolysis to cyanuric acid (Cason's "TM-2") occurred slowly at room temperature. A quantitative study of nitrous oxide evolution during hydrolysis at 90° gave equivalent weights of 175, 177, 178. This corresponds to the evolution of one mole of gas per mole of $C_3H_3O_4N_5$ and to the evolution of three moles on the basis of Cason's formula. Data on the sodium and potassium salts are given by Cason[3] whose formulas are three times the true molecular formulas.

We have repeated the nitration of triacetylmelamine at 5–10° and agree with Cason that the product is a salt of triacetylmelamine for it hydrolyzes rapidly at room temperature to triacetylmelamine hydrate.

We have extended Cason's nitration studies by examining the use of fuming nitric acid alone. Ten grams of triacetylmelamine was dissolved in 40 cc. of freshly distilled fuming nitric acid (d. 1.50) and after five hours at room temperature the solution poured on ice. After 30 minutes there was obtained 3 g. of a white solid which darkened and decomposed when heated to 300°. The substance was soluble in dilute sodium bicarbonate solution and could be precipitated again by acidification. When water solutions of the substance were warmed acetic acid was evolved and a typical ammeline–ammelide mixture (N, 49–55%) precipitated. Hydrolysis with hot dilute sulfuric acid gave cyanuric acid. The observed properties and analytical data are in accord with the identification of the substance as the **monohydrate of N-nitro-N′,N″-diacetylmelamine**. The hydrate character is consistent with the retention of two acetyl groups.

Anal. Calcd. for $C_7H_{11}O_5N_7$: C, 30.8; H, 4.03; N, 35.9. Found: C, 30.5, 30.3; H, 4.27, 4.12; N, 35.4, 35.9.

DURHAM, N. H.

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[5] D. J. Salley and J. B. Gray, THIS JOURNAL, **70**, 2650 (1948).

[6] G. F. Wright, *et al.*, *Can. J. Research*, **26B**, 89, 104 (1948).