question. The fact that no traces of *n*-butane are found in the reaction products supports the theory that isomerization preceeds cracking. The stability of neohexane under the conditions studied (expt. 22) indicates the opposite point of view.

Summary

1. Paraffin hydrocarbons (*n*-hexane, *n*-heptane and *n*-octane) when subjected to the action of aluminum chloride–hydrogen chloride at temperature of their boiling point or slightly above, are cracked to lower boiling isoparaffin.
2. Cracking with the production of isobutane is the predominant reaction.
3. Cracking consists in the dealkylation of paraffin and polymerization–depolymerization of the cracked fragments to produce isoparaffins.
4. The amount of dealkylation reaction is a direct function of catalyst concentration.
5. No destructive alkylation to form hydrocarbons boiling higher than the charge takes place under these conditions.
6. A reaction mechanism to explain the above facts is proposed.

CHICAGO, ILLINOIS RECEIVED MAY 20, 1946

[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

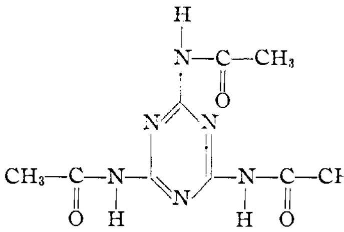
The Nitration of Melamine and of Triacetylmelamine[1]

BY JAMES CASON[2]

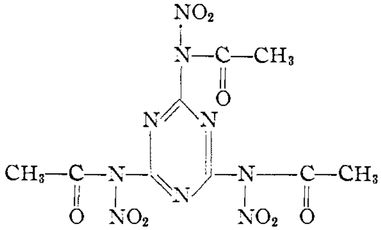
Melamine has been nitrated with nitric acid in acetic anhydride by Whitmore and co-workers,[3] but the product obtained was not purified and analyzed. We have repeated this preparation and have obtained the highly unstable nitration product in a crystalline condition by low temperature acidification of the purified sodium salt. Analyses of the nitration product, its sodium salt and its potassium salt indicate for the nitration product the formula $C_3H_{3-4}N_7O_5$. It will be noted that this substance contains only one nitrogen atom more than melamine but contains five oxygen atoms. The salts contain two atoms of metal and one molecule of water. On the basis of the evidence obtained nothing can be suggested concerning the structure of this compound.

In order to study the nitration of triacetylmelamine it was necessary to develop an improved method for preparing this substance. Although diacetylmelamine may be readily obtained by heating melamine with acetic anhydride, the triacetyl derivative is obtained only with difficulty. Ostrogovich[4] used 200 cc. of acetic anhydride for the conversion of 0.5 g. of melamine to the triacetyl derivative. By improvements in the procedure, including recycling the acetic anhydride it has been found possible to convert 120 g. of melamine to the triacetyl derivative in 99% yield, using only 450 cc. of anhydride. The difficulty of introducing the third acetyl group into melamine may be associated with the occurrence of a tautomeric change prior to acetylation[4,5]; however, it is also possible that the very low solubility of diacetylmelamine is responsible for this difficulty.

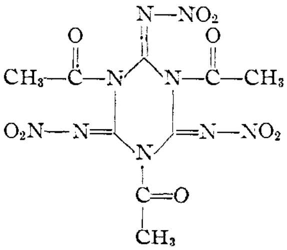
If triacetylmelamine has the structure, I, nitration with nitric acid in acetic anhydride would be expected to give the corresponding nitramide, II. Actually, the compound obtained when nitration was carried out at 20–25° did not have any of the properties that would be expected of II. This nitration product, which has been designated as TM-1, is too unstable to be purified, but analyses of the crude substance and of its stable sodium



I



II



III

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[1] This paper is based entirely on work done for the Office of Scientific Research and Development under Contract OEMsr-790 with Vanderbilt University.

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[3] Work carried out under the direction of Dean F. C. Whitmore at Pennsylvania State College under a contract with the Office of Scientific Research and Development.

[4] Ostrogovich, *Gazz. chim. ital.*, **65**, 566 (1935).

[5] McClellan, *J. Ind. Eng. Chem.*, **32**, 1181 (1940).

and potassium salts indicate the formula $C_9H_9N_{15}O_{12}$. The salts contain three atoms of metal and three molecules of water. On heating in water, TM-1 loses three molecules of nitrous oxide and gives a quantitative yield of another compound which has been designated TM-2.

Analysis of TM-2 indicates the formula $C_9H_9N_9O_9$, which corresponds to trinitrotriacetylmelamine; however, TM-2 is much more stable to hydrolysis than would be expected if its structure is that shown in Formula II. It was recovered unchanged after refluxing for three hours with $2N$ hydrochloric acid, also after heating for one hour at 65–70° with 98% nitric acid. After heating under reflux for two hours with 1 N sodium hydroxide, 80% of the starting material was recovered, and after twenty six hours most (but not all) of the material had been broken down to ammonium carbonate. TM-2 sublimes at a very high temperature, at atmospheric pressure, without melting or apparently decomposing.

TM-2 is insoluble in sodium carbonate solution but dissolves in excess sodium hydroxide. If the alkaline solution is made strongly acid unchanged TM-2 is precipitated; however, if the alkaline solution is titrated to a phenolphthalein endpoint there crystallizes a salt of TM-2 which contains three molecules of sodium hydroxide (or three atoms of sodium plus three molecules of water) per molecule of TM-2.

The persistence of the C_9H_9-unit in TM-1 and TM-2, and the extraordinary stability of TM-2 suggest that the triazine ring system is intact, but the properties of TM-2 are more consistent with Formula III than with Formula II. Such a formula explains the failure of triacetylmelamine to nitrate normally to a nitramide which would be saponifiable to a nitramine. The three nitrous oxide units in TM-1 may possibly be attached as rings at the carbon–nitrogen double bonds in Formula III.

No further investigation of these compounds is in progress.

Experimental[6]

Melamine was nitrated as described by Whitmore[3] by adding 5 g. of melamine, during twenty minutes, to a mixture of 50 cc. of acetic anhydride and 50 cc. of 98% nitric acid, stirred at 0–5°. After stirring an additional hour at this temperature, the precipitated material was collected and washed with acetic acid. After the precipitate had been stirred for three minutes with 150 cc. of ice–water, it was collected, washed and dried. The yield of a fine *white powder was 7.5 g. (87% on basis of formula below)*. No crystalline material could be obtained until after purification through the sodium salt.

For preparation of the **sodium salt**, 4.60 g. of crude nitration product was dissolved in 46 cc. of 5% sodium carbonate, by warming, and treated with Norit. On addition of 23 cc. of ethanol to the clear, pale greenish-yellow filtrate, crystallization of soft, fine needles set in. After two further crystallizations from 30–40% ethanol there was obtained 1.40 g. of soft, colorless needles. On drying *in vacuo* at 100° there was a loss in weight of 0.14 g. (corresponding to $2H_2O$ for the formula below); this water is regained on standing in air. The compound dried *in vacuo* was analyzed.

Anal.[7] Calcd. for $C_3HN_7O_5Na_2 \cdot H_2O$: C, 12.90; H, 1.08; N, 35.10; Na, 16.48. Found: C, 13.00; H, 1.26; N, 34.73; Na, 16.48.

For preparation of the **pure nitration product**, a 1.40-g. sample of the pure sodium salt was dissolved in 50 cc. of water, cooled in ice and treated with 15 cc. of 2 N hydrochloric acid (an amount equivalent to the sodium gives no precipitate). There crystallized immediately 1.10 g. of long colorless blades, which were collected at once and washed with ice–water, alcohol and ether. On standing for an hour at 5° in contact with the solution the blades disappear completely, most of the material dissolves and a small amorphous precipitate is left. The blades are not hygroscopic in air, and drying at 100° *in vacuo* caused no loss in weight.

Anal.[7] Calcd. for $C_3H_3N_7O_5$: C, 16.58; H, 1.39; N, 45.10. Found: C, 16.74, 16.09; H, 1.47, 1.27; N, 44.77, 44.75.

Even when mixed with cupric oxide this substance tends to explode on heating for combustion, hence the poor check on carbon. Combustion of a sample of crude nitration product directly from the reaction mixture gave C, 17.70; H, 2.22.

The **potassium salt** of the nitration product, prepared as described for the sodium salt, was crystallized twice from water. It forms very pale yellow iridescent blades. It lost no weight on drying at 100° *in vacuo*.

Anal. Calcd. for $C_3HN_7O_5K_2 \cdot H_2O$: K, 25.14. Found: K, 25.09, 25.29.

Acetylation of Melamine.[4]—In a preliminary experiment 3 g. of melamine was refluxed with 75 cc. of acetic anhydride for two minutes, then the acetyl derivative was filtered from the cooled solution; weight, 4.58 g. (91.5% of theoretical for the diacetyl derivative). When refluxing was continued for one hour the yield was 4.88 g. (98% for diacetyl compound). Kjeldahl determination of nitrogen in the latter sample indicates nearly pure **diacetylmelamine**.

Anal. Calcd. for $C_7H_{10}N_6O_2$: N, 39.97. Found: N, 39.28.

When a similar run was made with the addition of 0.50 g. of sodium acetate, and refluxing was continued for five hours the yield was 5.83 g. (97.2% for **triacetylmelamine**). For analysis, the product was crystallized twice from acetic acid.

Anal. Calcd. for $C_9H_{12}N_6O_3$: N, 33.31. Found: N, 33.10.

Triacetylmelamine was also prepared according to Ostrogovich[4] by heating under reflux a mixture of 1 g. of melamine with 400 cc. of acetic anhydride; N, 32.97. By either method of preparation, the substance is obtained from the reaction as small flakes and crystallizes similarly from acetic acid, in which it dissolves to the extent of about 2.5 g. per 100 cc. at boiling and about 0.5 g. per 100 cc. at 23°. Ostrogovich[4] reported the m. p. as 298–300 . but our product darkened somewhat without melting at 310°.

For larger-scale preparation of triacetylmelamine, a mixture of 30 g. of melamine, 5 g. of sodium acetate and 450 cc. of acetic anhydride was placed in a 1-liter round bottom flask fitted with a tantalum wire Hershberg stirrer[8] inserted through a short reflux condenser attached with a ground joint. This mixture was heated in an oil-bath and stirred under reflux for six hours. As soon as the solution boils the insoluble melamine changes to diacetylmelamine, which is so voluminous that the mixture becomes pasty. This gradually changes to the triacetyl derivative which consists of soft, shiny flakes. After cooling the reaction mixture in the refrigerator overnight the product was collected, drained well and washed with 20 cc. of acetic acid (to remove sodium acetate) which

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(6) All melting points are corrected.

(7) Dumas analysis for nitrogen by the Arlington Laboratories.

(8) Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

was added to the filtrate. The filtrate was then removed and the product was washed with an additional 30 cc. of acetic acid and two portions of ether.

To the filtrate was added 30 g. more melamine, and the mixture was treated as before. This process was repeated until five 30-g. lots of melamine had been processed. The results are tabulated.

TABLE I

Lot	Yield, g. (%)	% Nitrogen (calcd., 33.31)
1	59.0 (98.3)	33.08
2	59.8 (99.6)	33.28
3	59.5 (99.2)	33.41
4	59.2 (98.7)	33.49, 33.40
5	57.2	34.86

Lots 1–4 were considered essentially pure triacetylmelamine, yield 237.5 g. (99%). The analysis of lot 5 indicates that it contains about 22% of the diacetyl derivative.

Triacetylmelamine is not hygroscopic in moist air, but when it is stirred with water it rapidly changes to voluminous, soft white crystals of the **monohydrate**, which does not lose water at 100° under 35 mm. pressure.

Anal. Calcd. for $C_9H_{12}N_6O_3{\cdot}H_2O$: N, 29.69. Found: N, 29.95.

Nitration of Triacetylmelamine.—A mixture of 25 cc. (37.5 g., 0.595 *M*) of 98% nitric acid and 22.5 cc. (24.3 g., 0.24 *M*) of acetic anhydride was treated with 10 g. (0.04 *M*) of triacetylmelamine during about three minutes, while the temperature was maintained at 10–20°. The acetyl derivative dissolved almost immediately, and if the temperature was below 15° another material crystallized in small amount. This precipitate redissolved immediately as the temperature was raised. The mixture was stirred for five hours at 25–28°, crystallization of a white product setting in after about forty minutes.

The crystallizate was collected directly on a sintered glass funnel and washed with acetic acid and ether; weight, 6.4 g. Treatment of the filtered reaction mixture with 50 cc. of anhydrous ether gave a small (0.6 g.) crystallizate on standing overnight at −5°. This seems to be the same as the original crystallizate. Drowning of the filtrate in ice–water gives no precipitate.

A few variations of the above conditions have been tried: (1) Stirring the reaction mixture for only two hours at 25–28° gives a yield of only 1.7 g. (2) Stirring for six and one-half hours at 19–21° gives a yield of 5.7 g. (3) Use of 12 moles (per mole of triacetylmelamine) of nitric acid and 4.5 moles of acetic anhydride gives a yield of 5.9 g. (4) Stirring for two hours at 5–10° gives a clear solution, and on addition of 50 cc. of anhydrous ether there separates a gummy precipitate which crystallizes on standing at −5°; weight, 9.5 g. This substance has been investigated only briefly but seems to be a salt of triacetylmelamine.

The material obtained at 25°, which has been termed TM-1 for convenience, dissolves to a limited extent in boiling acetic acid or nitromethane, but no crystallization occurs on cooling and long standing. It is somewhat soluble in cold water and dissolves readily in 10% sodium carbonate with evolution of carbon dioxide. It decomposes without melting. Since no means of purification have been discovered the crude substance was investigated.

Titration of this substance with standard alkali gives values of doubtful significance, for the solution is very highly buffered at the end-point. Two samples of crude TM-1 were analyzed (thorough mixing with cupric oxide is necessary to avoid explosion on heating for combustion).

Anal. Calcd. for $C_9H_9N_{15}O_{12}$: C, 20.82; H, 1.76. Found: C, 19.42, 19.76, 20.69; H, 1.99, 1.87, 1.98.

The **sodium salt of TM-1** was prepared by dissolving 3.00 g. of the substance in 15 cc. of warm 10% sodium carbonate solution. On cooling in the refrigerator, 2.00 g. of salt crystallized. After two crystallizations from water it was obtained as well-formed, feathery blades.

Anal.[7] Calcd. for $C_9H_6N_{15}O_{12}Na_3{\cdot}3H_2O$: C, 16.91; H, 1.89; N, 32.88; Na, 10.79. Found: C, 16.98, 17.18; H, 2.03, 1.97; N, 32.34, 32.44; Na, 10.43, 10.66.

For combustion analysis, the substance was burned successfully in a mixture of potassium dichromate and cupric oxide.

This sodium salt is relatively stable in hot water and may be conveniently crystallized from water; however, if TM-1 is warmed with ammonium hydroxide or ammonium carbonate decomposition with evolution of gas occurs, and an amorphous, water-insoluble product is obtained.

Potassium Salt of TM-1.—A 3.00-g. sample of TM-1 was dissolved in 30 cc. of boiling 7% potassium carbonate. On cooling there crystallized 2.2 g. of iridescent needles. After two further crystallizations from water and drying *in vacuo* at room temperature, the substance was dried, for analysis, at 100° under 14 mm. pressure. Loss in weight was 7.19% ($3H_2O$ corresponds to 7.25%).

Anal. Calcd. for $C_9H_6N_{15}O_{12}K_3{\cdot}3H_2O$: K, 17.04. Found: K, 16.87.

On treatment with water, TM-1 suffers decomposition with loss of a colorless gas. The decomposition is complete in about five minutes at 95–100°, but requires several days at room temperature or below. When an aqueous solution of the sodium salt of TM-1 is acidified the solution remains clear at first. During a period of one or two days there slowly separates the compound described below (TM-2).

Preparation of TM-2.—A 5.96-g. sample of TM-1 was heated in 25 cc. of water. During three to four minutes there was collected, over water at 50°, about 1200 cc. of gas (calcd. for $3N_2O$ at S. T. P., 770 cc.). This gas had the mild but acrid odor of nitrous oxide, and a glowing splint dropped into it burst into bright flame. After cooling the residual aqueous solution, 4.21 g. of TM-2 was collected. Since the solubility of TM-2 in 25 cc. of water is 0.15 g., total recovery of TM-2 was 4.36 g. (calcd., 4.45 g.).

Anal.[7] Calcd. for $C_9H_9N_9O_9$: C, 27.92; H, 2.34; N, 32.54. Found: C, 27.79, 27.74; H, 2.50, 2.49; N, 32.04, 32.19.

Sodium Salt of TM-2.—A 1.000-g. sample of TM-2 was dissolved in 50 cc. of 0.5155 *N* sodium hydroxide. Titration with standard acid to a phenolphthalein end-point showed the consumption of 3.0 equivalents of base; there rapidly crystallized 1.068 g. of long blades. This substance lost no weight on drying *in vacuo* at 100°.

Anal. Calcd. for $C_9H_9N_9O_9{\cdot}3NaOH$: C, 21.27; H, 2.36; Na, 13.61. Found: C, 21.08; H, 2.46; Na, 13.32.

On acidification of a suspension of 108 mg. of this salt there was obtained 72 mg. of TM-2, identified by analysis.

Attempts at Cleavage of TM-2.—A 3.00-g. sample of TM-2 was dissolved in 100.0 cc. of 0.9844 *N* sodium hydroxide. Aliquots of 10.00 cc., titrated after thirty minutes at 50, 65, 75 and 90°, required respectively 3.61, 3.59, 3.57 and 3.59 cc. of 2.046 *N* hydrochloric acid. In each case, the salt of TM-2 crystallized at the end-point. A 10-cc. aliquot titrated after two hours heating under reflux required 3.40 cc. of acid and the salt crystallizing weighed 0.30 g. (77% yield). After twenty-six hours of heating under reflux, considerable ammonium carbonate had collected in the condenser, and the recovery of salt after titration (2.36 cc.) was 0.043 g. To another 10-cc. aliquot, after the twenty-six-hour heating period, a full equivalent of acid was added, and the precipitate was crystallized from water, after filtration from silica. Recovery of TM-2, 20 mg., analysis: C, 27.74; H, 2.60.

A 2.00-g. sample of TM-2 was heated under reflux for three hours with 50 cc. of 2 *N* hydrochloric acid, not all the TM-2 dissolving. From the cooled solution there was recovered 1.85 g. of crystalline TM-2, analysis: C, 27.73; H, 2.30.

A 5.00-g. sample of TM-2 was stirred with 10 cc. of 98% nitric acid at 65–70° for one hour. After addition of ice and water, the white precipitate was collected, weight 4.40 g., analysis: C, 28.31; H, 2.65.

Summary

There has been isolated from the nitration of melamine a product of the empirical formula, $C_3H_{3-4}N_7O_5$. A convenient procedure for the preparation of triacetylmelamine has been developed, and by nitration of this compound there has been obtained a compound whose formula is $C_9H_9N_{15}O_{12}$. By heating this compound in water, there has been obtained another compound, $C_9H_9N_9O_9$. Salts of these three new compounds have been obtained, and some of their properties have been determined, but their structures have not been elucidated. A possible structure for the compound, $C_9H_9N_9O_9$, has been suggested.

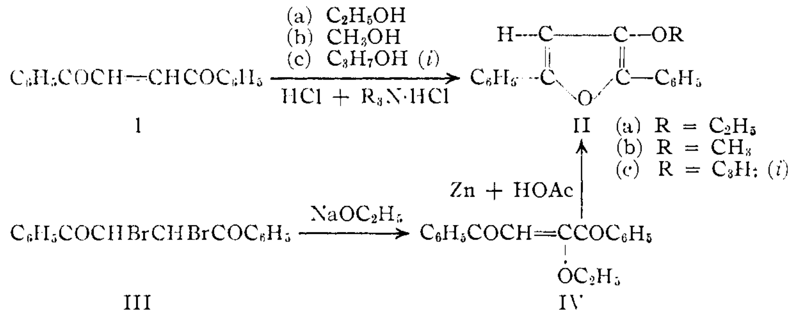
NASHVILLE, TENN. RECEIVED OCTOBER 3, 1946

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS AND THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

The Reaction of Alcohols with Dibenzoylethylene

BY PHILIP S. BAILEY AND ROBERT E. LUTZ

Ethanol, methanol and *i*-propanol have been found to react with dibenzoylethylene (I) under slightly acidic conditions in the presence of secondary or tertiary amine salts. The product in each case was the corresponding 2,5-diphenyl-3-alkoxyfuran (II). Although the yields were low (around 13%), it is of interest that such a reaction occurs under the conditions employed.



The ethoxy and *i*-propoxyfurans (IIa and IIc) are new compounds. The structure of the former was proved by synthesis along another path; namely, reaction of dibenzoyldibromoethane (III) with sodium ethoxide to yield IV, followed by reductive cyclization to IIa. The methoxyfuran (IIb) had previously been prepared in the same way.[1] Attempts to prepare the *i*-propoxyfuran (IIc) by this method failed in the first step, namely, treatment of dibenzoyldibromoethane (III) with sodium *i*-propoxide, which led to resin formation. There can be little doubt as to the structure of the compound, however, since it was obtained in a reaction identical with those which yielded the corresponding methoxy and ethoxy furans. The new reaction constitutes the only way by which the *i*-propoxy compound (IIc) (and perhaps other higher ethers) can be prepared at the present time.

The conditions under which the alcohol addition reactions occurred were quite specific and involved the presence of an amine hydrochloride and enough hydrogen chloride to show a *p*H of 2–3 when indicator paper was dipped into the reaction mixture. When either the amine hydrochloride or the hydrogen chloride was omitted, the reaction could not be detected. An increase in hydrogen chloride concentration tended to eliminate the formation of the alkoxyfurans and increase the formation of by-products. Replacement of the amine hydrochloride with alcohol-soluble inorganic salts (lithium chloride or magnesium chloride, all other conditions remaining the same) gave negative results. Negative results were also obtained when ammonium chloride was used, but this might have been due to its low solubility in alcohols. The high specificity of these conditions is perhaps not surprising in view of the low yield at best and of the many competing reactions which are possible.

In these reactions there was obtained along with the furans a mixture from which two colorless, high-melting substances were isolated. These were obtained also in several experiments which produced no furan. These new compounds of composition close to that of dibenzoylethylene are under investigation.

The addition of alcohols to α,β-unsaturated esters[2] and ketones (dibenzoylacetylene)[1] has been carried out in the presence of a sodium alkoxide catalyst. In the present work, however, such a process led to resinification. Under somewhat different conditions, fulvenes have been obtained by the treatment of dibenzoylethylene with sodium ethoxide.[3]

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[1] Conant and Lutz, THIS JOURNAL, **47**, 881 (1925).

[2] Purdie and Marshall, *J. Chem. Soc.*, **59**, 468 (1891); Rehberg, Dixon and Fisher, THIS JOURNAL, **68**, 544 (1946).

[3] Gardner and Rydon, *J. Chem. Soc.*, 48 (1938); Fuson, Fleming, Warfield and Wolf, *J. Org. Chem.*, **10**, 121 (1945).